INTRODUCTION TO CHEMISTRY

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D. S. MACNAIR

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AN INTRODUCTION TO CHEMISTRY

BY

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PREFACE

THIS book is intended to provide a laboratory course for beginners in chemistry—more particularly for pupils in secondary schools. It is desirable, though not absolutely necessary, that pupils using it should have previously gone through a course of practical work in measurements of area, volume, mass, density, etc., and should have at least a qualitative knowledge of the behaviour of gases to changes of pressure and temperature. The treatment adopted differs from that of most of the elementary text-books of the science. The aim of the author has been to lead the student by means of a connected series of simple experiments, *each of which is suggested by what has gone before and forms a link in a chain of reasoning*, to a knowledge of some of the most important principles of the science, to an understanding of some of the commonest of the phenomena which surround him in everyday life, and to an appreciation of the aims and methods of scientific research. It is hardly necessary to say that the experiments, or at least a large proportion of them, should be performed by the pupils individually. The importance of individual practical work is now fully recognised—indeed, there is nowadays some danger of too exclusive attention being given to practical work and too little to the constant questioning and discussion of results which ought to accompany it, and without which it may become almost as formal and soulless an exercise as the learning of lists of irregular verbs. A few experiments which require somewhat expensive apparatus, or which would be dangerous for beginners, have been specified as intended to be performed by the teacher only. The rest

are all within the capabilities of boys of fourteen or fifteen, and should, as a rule, be performed by the whole class. Care has been taken to keep the apparatus as simple as is consistent with accurate results, and it is hoped that the illustrations, nearly all of which have been specially drawn from photographs of the actual apparatus, will be found a reliable and useful guide to the teacher whose experience in the fitting up of apparatus is limited. A few of the experiments are new—at least to elementary text-books—and in several cases modifications have been suggested in the methods of carrying out well-known experiments which it is believed will be found to be improvements. As examples, the method of finding the quantitative composition of chalk described on pp. 73 and 74, the volumeter (p. 92), and the method of decomposing water by burning magnesium in steam (pp. 53 and 54) may be cited.

No attempt has been made to divide up the work into lessons or to indicate the time to be spent on the various sections, for this will vary in every school according to the ability of the pupils and the amount of time allotted to the subject. In schools where only three or four hours weekly are given to chemistry (and this is the minimum time for satisfactory work) it will probably be found that the first seven chapters will give sufficient material for a session's work. Where more time is given, the rate of progress will be correspondingly more rapid. It will be noticed that although no reference has been made to the atomic theory, formulæ and equations have been introduced in chapter ix. and have been freely used in the later chapters—not as expressing molecular changes, *but solely as a shorthand expression of the proportions by weight in which the elements are found by experiment to combine.* This use of equations is entirely independent of the atomic theory (Dalton's formulæ and equations were used by many of his contemporaries and successors who rejected his theory of atoms *in toto*), and it has such enormous advantages in assisting the memory, in bringing out analogies

between different classes of reactions, and in expressing the results of quantitative experiments in a form at once compact and easily comprehensible, that no intelligent teacher of chemistry who goes beyond the earliest steps can afford to reject it. That some teachers do so, and actually spend months on the teaching of the law of equivalent proportions without daring to introduce so much as the formula H_2O for water is probably due to a confused notion (for which encouragement may be found in many text-books) that an equation can have no meaning apart from what it implies as to the molecular constitution of the reacting substances.

The author's best thanks are due to his friend and former colleague, Mr D. E. Jones, B.Sc., for his kind assistance and for many valuable suggestions.

EDINBURGH, *June* 1902.

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INTRODUCTION TO CHEMISTRY

CHAPTER I

INTRODUCTORY

1. **Physical and Chemical Changes.**—In the study of physics we have often to investigate changes which take place in the form or the properties of matter. For example, the change of solid ice to liquid water, and finally to an invisible gas (steam), is typical of a kind of change which is produced in a great number of substances by the action of heat. Again, the changes in properties which occur when a steel wire is magnetised, or when a glass rod is rubbed with silk, are examples of another class of changes which you may have already studied. In all these cases, although the properties (and very often the appearance also) of the substance are altered, its *composition* remains unchanged. We can always get water again from ice by heating or from steam by cooling it. The magnetised needle and the electrified glass rod still remain steel or glass respectively, although they have acquired the additional property of attracting certain other substances. But there are other cases of change in the properties of matter which differ essentially from these. For example, when a clean iron surface is exposed to moist air it gradually becomes dull; after a while you can remove from its surface "iron rust" in the form of brownish flakes or powder. The hard shining metal is gradually but surely changed into a brown brittle substance: it not only acquires new properties, but it loses its original properties and becomes an entirely new substance, differing in colour, hardness, lustre, conducting power for heat and electricity, specific gravity and fusibility from the original metal. The conversion of metallic iron into iron rust is an example of *chemical change*, and is distinguished from the merely *physical* changes already referred to by its deep-seated character and by the fact that it involves (as you will find later on from your own experiments) not only a

change in the properties of the substance, but also a change in its composition. Many other examples of such deep-seated "chemical changes" might be given. We may here mention those that occur when animal and vegetable substances are heated, or exposed for a long time to the air, when limestone is converted by heat into quicklime, or when gunpowder is ignited.

The differences between physical and chemical changes may be further illustrated by the two following experiments :—

Ex. 1.—Put a globule of mercury the size of a pea into a clean and perfectly dry test-tube, and heat it cautiously in the flame of a Bunsen burner or spirit-lamp. The mercury soon boils, and the lower part of the tube is filled with a colourless invisible vapour. Remove the tube from the flame, allow it to cool, and then examine it with a pocket lens. Note that although the mercury is now spread over a large surface instead of being collected into a single globule it has regained its original properties, the physical change produced by heat having lasted only so long as the higher temperature was kept up. Now repeat the experiment with another test-tube containing a small piece of sulphur. Note that in this case also heat produces changes, the sulphur being converted first into a yellow liquid, then into a dark brown viscous substance like treacle, and lastly into a brown gas. Allow to cool, break the tube,[1] and convince yourself that these changes were temporary only and that the sulphur has now regained its original properties. Lastly, take another globule of mercury in a clean, dry test-tube, add about twice its bulk of sulphur, and heat

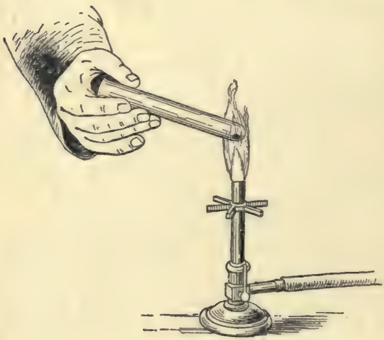

Fig. 1.

[1] For this and other similar experiments it is convenient to use very small test-tubes (about 4 ins. × ½ in.). These can be bought for from 2s. to 3s. per gross.

carefully. Note that in this case the contents of the tube suddenly become red-hot, showing that heat is being evolved within the tube by the interaction of the sulphur and mercury. When no further change takes place allow the tube to cool, shake out the contents, and compare the properties of the new substance ("sulphide of mercury") with those of the two bodies from which it was produced. You will find that you have now a new substance entirely distinct from either mercury or sulphur.

The changes produced by heat in either mercury or sulphur alone are *physical* changes: they are temporary and produce no alteration in the composition of the substance. But the change that occurs when hot mercury and hot sulphur are brought together is a *chemical* change, for in this case an entirely new substance is produced, differing in composition and in all its properties from both the mercury and the sulphur by whose union it was formed.

Ex. 2.—Place a few crystals of silver nitrate in a clean dry test-tube and heat them cautiously in the Bunsen flame. Notice the physical change which is first brought about—the crystals fuse to a clear liquid. Convince yourself that the change is merely physical by allowing the liquid to cool. What happens?

Now heat the contents of the tube more strongly until no further change takes place. Notice the evolution of a heavy dark red gas. Break the tube, and examine the substance left behind. In this case the change is clearly a chemical one: the white crystals of silver nitrate have been converted into two substances, each of them distinct and quite different in properties from the original crystals—the one a reddish gas, the other a hard white substance which can be shown to be metallic silver. In this experiment heat has produced both kinds of change. First, at a comparatively low temperature the temporary, *physical* change from the solid to the liquid form; then at a much higher temperature the permanent change into two new kinds of matter—a typical example of a *chemical* change.

2. Elements and Non-Elements.—The last experiment is a good example of the particular kind of chemical action which is called *decomposition*, or the breaking up of a single substance into two or more different kinds of matter. Such changes are

generally brought about by the action of heat or electricity. During many centuries chemists have attempted to decompose every kind of matter within their reach, and in the great majority of cases their attempts have been successful. Of all the thousands of different materials found in the earth and in the bodies of plants or animals, or prepared artificially, only about seventy have resisted the efforts of the chemists to break them up into simpler bodies. To these substances is given the name **Element** (from the Latin *elementum*, a first principle), and from their interaction all other kinds of matter can be built up.

Ex. 3.—*To examine the action of heat on various substances.* — Heat separately in clean dry test-tubes of narrow bore small fragments of the following substances: — Nitre, silver, sugar, salt, sodium bicarbonate ("baking soda"), water, bread, wood, lead, iodine. Observe carefully what takes place in each case, and record your results. Lastly, draw what inferences you can as to whether the substances are elements or not. Remember that you can draw no positive inference except when the substance is clearly split up into two or more new bodies. If it seems to be unchanged, this is no proof that it is an element, for you have tried only one way of decomposing it out of many. In order to avoid soiling the sides and so making it difficult to observe what happens within the tube, the solid should be placed at the end of a long, narrow gutter of paper. This is held horizontally and slipped into the tube, which is then turned into the vertical position: the paper may now be withdrawn, leaving the solid at the bottom and the sides of the tube clean.

The following is a list of the most important chemical elements, and includes all that are commonly met with or are of great practical importance. (A fuller list will be found on p. 98):—

Aluminium	Chlorine	Lead	Platinum
Antimony	Chromium	Magnesium	Potassium
Arsenic	Copper	Manganese	Silver
Barium	Fluorine	Mercury	Silicon
Bismuth	Gold	Nickel	Sodium
Boron	Hydrogen	Nitrogen	Sulphur
Calcium	Iodine	Oxygen	Tin
Carbon	Iron	Phosphorus	Zinc

Remember that we cannot say for certain that these substances are *incapable* of being broken up into simpler bodies, but only that so far no one has succeeded in so breaking them up. It is quite possible that some of the substances in this list may yet be proved to be made up of two or more constituents, though at present this does not seem probable.

3. Mixtures and Non-Mixtures.—So far we have classified all substances into elements and non-elements. But there is another obvious way of classifying substances which we must notice—namely, that into **mixtures** and **non-mixtures** or pure substances. In many cases we can tell at once by the eye that a substance is a mixture. For example, a careful examination of a piece of granite will show that it is a mixture of at least three different minerals, each of which can be distinguished by its special properties: the black flakes, easily scratched or split up by a knife, are mica; the dull white crystals are felspar; and the glassy transparent particles, too hard to be scratched, are quartz.

On the other hand, the particles of quartz, though differing from each other in shape, have all the same properties, and even when examined by the microscope are found to be homogeneous. Quartz, then, is a pure substance, or a "chemical individual"; in other words, it is not a mixture, and cannot be separated by any mechanical means into two different kinds of matter. (We shall find later that it can be separated by *chemical* means, and that it is therefore a compound, not an element.) Most naturally occurring substances are mixtures, but it is not always easy to say whether a given substance is a mixture or not. When the particles are too fine to be seen by the naked eye, the microscope will still show, in many cases, whether we have to do with a single substance or a mixture. Not always, however, and where the microscope fails us we must have recourse to other means. And it is evident that when the different kinds of particles can be seen only by the aid of the microscope, it would be hopeless to try to separate the constituents of the mixture by the tedious process of picking out the individual particles. The different methods by which mixtures can be recognised and separated into their constituent parts will form the subject of our next chapters.

CHAPTER II

SOLUTION AND CRYSTALLISATION

4. Action of Water on Salt.—If a little common salt be thrown into water, you know that after a little while the salt will disappear. So far as can be *seen* the salt has ceased to exist, but you know that it is not destroyed, for the water will now have a salt taste. Let us see whether the salt is permanently altered by the change that has taken place.

Ex. 4.—Take a clean, dry porcelain basin, weigh it along with a short glass rod, and note the weight. Now add five or six grammes of salt, and weigh again. Add 10 c.c. of distilled water, and weigh again. Stir till all the salt has disappeared or **dissolved**. We have now a **solution** of salt in water. Does any alteration in weight occur when the salt dissolves?

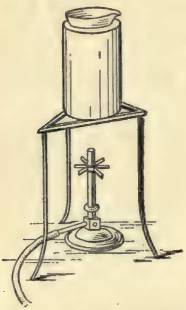

Fig. 2.—Evaporating a liquid on the water-bath.

Now place the basin on a water-bath[1] (Fig. 2), and evaporate off the water. A white residue is left. When all the water seems to be gone remove the basin from the water-bath, dry the outside carefully, allow it to cool, and weigh it once more. To make sure that the contents of the basin are really dry replace it on the water-bath for ten minutes, and weigh again. If the two last weighings agree we may be sure that all the water is gone; if not, the heating and weighing must be repeated, until further heating produces no alteration in the weight.

Finally, compare the weight of the residue with that of the salt originally taken. What do you find?

5. Solubility.—If we add salt in small quantities at a time

[1] A tin can with a rather narrow opening answers very well.

to a little water, shaking up after each addition, we find that at first the salt dissolves quickly, afterwards more and more slowly, till at last a point is reached when no more will dissolve. The solution is then said to be **saturated.**

Ex. 5. — *To find the solubility of common salt.* — By means of a pipette measure out 50 c.c. of distilled water into a small flask. Weigh out 25 grammes of powdered common salt on a basin or clock-glass, and add it in small portions to the water, shaking vigorously after each addition, until the point is reached when a little salt remains undissolved even after prolonged shaking. Now weigh the salt left in the basin, and subtract its weight from the weight originally taken—the difference gives approximately the weight of salt that can be dissolved in 50 c.c. of water at the temperature of the laboratory.

A more exact result (why?) may be got thus: Allow the saturated solution to stand until the undissolved salt has settled to the bottom, leaving a clear "supernatant" liquid. Now draw off 10 c.c. of this liquid with a pipette, and place it in a clean, dry porcelain basin, which has been previously weighed. Weigh again (what does the result tell you as to the density of the solution?), and then evaporate exactly as in the last experiment, and weigh the salt that remains. By subtracting its weight from that of the solution we find the weight of the water in which it was dissolved, and from this we can easily calculate the weight of salt that can be dissolved by 100 grammes of water at the temperature of the laboratory. (The temperature should be carefully noted.)

From this experiment we see that in the case of salt the weight that can be dissolved by a given weight of water at a given temperature is quite definite. The same is true of other substances, as can be readily shown by experiment. The amount varies very widely for different substances, as the following experiments will show.

6. Ex. 6.—*To show that different substances have different solubilities.*—Put a little plaster of Paris into a small glass beaker, add water,[1] and stir. The water at once becomes

[1] In this and all future experiments the water used must be *pure*. If the tap-water is hard or otherwise impure it will be necessary to provide distilled water.

milky, and even if we add a large quantity the plaster of Paris *seems* to remain undissolved. But perhaps some of it has dissolved. In order to decide, we must get rid of the undissolved and "suspended" powder, either by allowing it to settle and then drawing off the clear liquid, or, more quickly, by filtering. To do this, take a circular piece of filter paper (good white blotting-paper will do), fold it into a semi-circle, and then again into a quarter circle. You will find that you can now open out the paper into a conical bag, of which one side has three thicknesses of paper and the other only one (see Fig. 3). Put the paper cone into a glass funnel, pressing it down with the fingers so that it may fit tightly, and moisten it with a few drops of water from a wash-bottle. (Fig. 4. See Appendix for directions for making this useful piece of apparatus.) Now pour the milky liquid into the filter, taking care that it does not go above the edge of the paper. A clear liquid passes through and must be collected in a clean beaker. This clear liquid is called the "filtrate." We have now got rid of the undissolved powder; but we do not know yet whether the liquid contains anything dissolved in it, or is merely pure water. How are we to find this out? Clearly by the same method that we have already used in the last experiment. Put a little of the solution into a clean glass basin or clock-glass, and evaporate to dryness on the water-bath. It will be found that a small quantity of a white residue is left, showing that some of the plaster of Paris has dissolved. Repeat the experiment, using a weighed [1] quantity

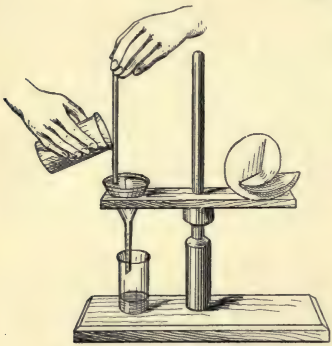

Fig. 3.—Filtering a liquid.

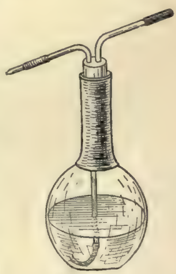

Fig. 4.
Wash-bottle.

[1] In this experiment, as in most of those in the book, the weights should be determined to the nearest milligramme. But teachers are recommended

of the liquid, and so determine the "solubility" of plaster of Paris—*i.e.* the number of grammes that will dissolve in 100 grammes of water. But it may be asked, "How do we know that the plaster of Paris dissolves as a whole? May it not be that the portion which has dissolved is different from that left on the filter paper?" To answer this we must try the experiment over again, using the undissolved powder and a fresh quantity of pure water. So long as some of the powder remains undissolved (*i.e.* so long as the solution got is *saturated*) we shall get exactly the same result as at first.

Determine in the same way the solubility of the following substances:—Sulphur, potassium chlorate, slaked lime, nitre, —using cold water, and noting the temperature of the room[1] during the experiment.

It will be found that each substance has its own definite capacity for dissolving, or *solubility* in water, and that the solubilities of different substances are very different. These differences frequently enable us to separate two substances that are mixed together, even when the mixture is so intimate that to the eye the substance appears perfectly homogeneous.

7. Ex. 7.—*To determine whether gunpowder is a mixture or a non-mixture.* — Put a few grammes of gunpowder into a test-tube, add twice its bulk of water, boil for two or three minutes, allow the undissolved gunpowder to settle, and pour the liquid through a filter, collecting the clear filtrate in a clean porcelain basin. Again add water and repeat the process, but this time pour the undissolved powder as well as the liquid on to the paper. Evaporate the filtrate on the water-bath. What does the residue look like? Try the effect of heating a little of it on platinum foil in the Bunsen flame: does it burn? Clearly

not to provide weights smaller than 1 centigramme; the third decimal should be got either by observation of the swings of the pointer, or by the use of a rider or sliding weight weighing 1 centigramme. These riders are easily made from thin aluminium wire. The length of wire that weighs 1 centigramme should be determined once for all, after which new riders can be made by measuring off the proper length of wire. It is not necessary that the beam of the balance should be graduated: the position of the rider can be estimated with sufficient accuracy after a little practice.

[1] As the solution of a solid usually causes a fall in temperature, care must be taken that sufficient time is allowed to permit of the solution acquiring the temperature of the room before drawing off the portion to be evaporated.

the white crystalline residue is quite different from the original gunpowder.

While the solution is being evaporated, turn to the undissolved residue on the filter paper. In order to get it pure we must first get rid of the small quantity of soluble matter that still clings to it. To do this the filter is "washed" by directing a stream of water from the wash-bottle round the *edge* of the paper. This water is allowed to drain away completely, and then a second "washing" is given in the same way, and the process is repeated until a few drops of the filtrate when evaporated on a piece of clean platinum foil leave no visible residue. When this is the case, the funnel, with the moist filter, is placed in an air-bath,[1] or supported at a height of ten inches or so over a small gas flame until the paper is perfectly dry. The black powder left on the paper is the *insoluble* portion of the gunpowder, and is clearly a different substance from the white crystals left in the basin. Heat a very little of it on a porcelain crucible lid. What happens? [Preserve the rest of the powder for another experiment.]

By means of water, then, you have been able to separate the gunpowder into two different kinds of matter—one a white powder, soluble in water, incombustible, melting to a colourless liquid when heated; the other a black powder, which is quite insoluble in water and takes fire readily, burning slowly with a blue flame like that of sulphur. We have not actually *proved* that gunpowder is a mixture of these two, for it is possible that some chemical change may have taken place on the addition of water to the gunpowder. If not, we ought to get gunpowder once more by thoroughly mixing the black powder and the white crystals in the proper proportions. Try this, and you will find that the mixture behaves like the original gunpowder —*i.e.* it burns rapidly when a light is put to it.

8. Solubility at Different Temperatures.—So far we have considered the solubility of substances in cold water only. But you know that sugar dissolves far more quickly in hot tea than in cold lemonade, and the same may be true of other substances. Experiment shows that in most cases the solubility increases with the temperature.

Ex. 8.—*To show the influence of temperature on solu-*

[1] See note on p. 82.

bility.—Make a cold saturated solution of copper sulphate ("Blue Vitriol") by shaking some of the powdered substance with cold water in a large test-tube. Make sure that the solution is saturated by pouring off the clear liquid into a clean dry test-tube and trying whether it has any action on another pinch of the blue powder. If the solution is really saturated the powder will of course sink to the bottom of the tube and remain undissolved. Now try heating the tube. (Care must be taken not to heat the glass, *except where it is wetted by the liquid.* The tube should be held in a slanting position with only the lowest half-inch of its length in the flame of the Bunsen burner or spirit lamp, and it should be constantly shaken so as to keep the sides of the tube wet. The fingers may be protected by folding a strip of doubled paper round the upper part of the tube. See Fig. 5.) You will find that the copper sulphate will now dissolve readily, and that, when the solution is boiling, you may add quite a large quantity of the copper sulphate before the solution again becomes saturated and refuses to dissolve any more. When this point is reached add to the solution an equal bulk of hot water, pour it into a clean porcelain basin, and put it aside to cool.

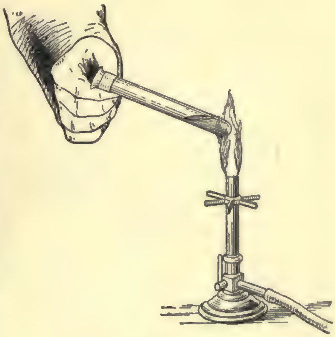

Fig. 5.

From this experiment we see that the solubility of a substance may vary very much according to the temperature. The great majority of solids are, like copper sulphate, more soluble in hot than in cold water; but there are some exceptions.

Ex. 9.—Repeat the last experiment, using nitre, plaster of Paris, and common salt successively instead of copper sulphate. What do you find as to the influence of temperature on the solubility of each?

Ex. 10.—*To find the solubility of common salt at* 50° *C.*—Support a large metal can or basin on a tripod stand. Put into it two or three litres of water, heat the water by a Bunsen

flame to 50° C, and try to regulate the flame so that the temperature remains constant. Now put into a flask about 200 c.c. of hot water and 100 gm. of powdered salt. Immerse the flask in the hot water and keep it there, with frequent shaking, for at least twenty minutes, taking care meanwhile to keep the thermometer as nearly as possible exactly at 50° C. Weigh carefully a small porcelain basin and a watch-glass that covers it. Pour into it about 10 c.c. of the clear solution from the flask (take care that no undissolved salt goes with it) and at once cover the basin with the watch-glass. Allow to

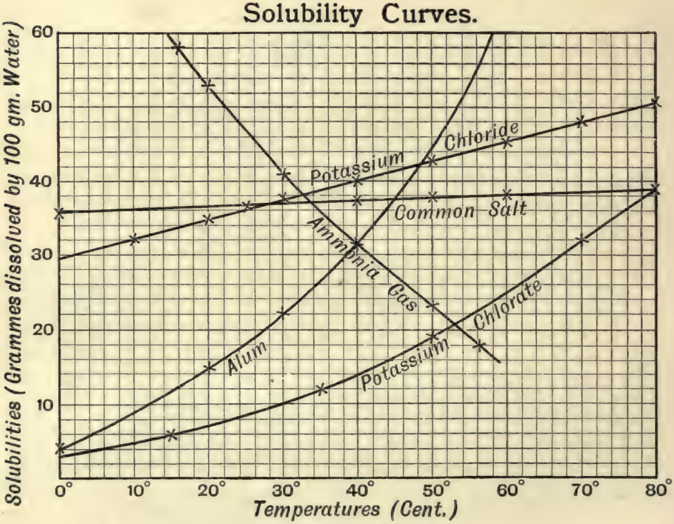

Fig. 6.

cool and weigh again. Now evaporate the solution to dryness as in Ex. 5, and find the weight of salt that dissolves in 100 gm. of water at 50° C.

Definition of Solubility.—*The solubility of a substance in water at a given temperature is expressed by the number of grammes of the substance which can be dissolved by* 100 *gm. of water at that temperature.*

Solubility Curves.—The results of experiments like the last

are best expressed graphically on squared paper as in the diagram (Fig. 6). In this diagram distances from the origin along a horizontal axis represent temperatures, while distances up a vertical axis represent solubilities (*i.e.* grammes of the solid that dissolve in 100 gm. of water). The result of each experiment at a particular temperature is plotted on the squared paper, and through the points thus found a curve is drawn which is called the "solubility curve" of the particular substance.

[*Note to Teacher.*—The making of one or two solubility curves is a useful class exercise. Four or five temperatures should be chosen, ranging from 0° to 50° C., and several pupils should be told off to make experiments at each temperature. It is not advisable to go beyond about 50° C., nor to use substances which are extremely soluble. The following substances are suitable:—potassium chlorate, potassium chloride, sal ammoniac, barium nitrate, lead nitrate, potassium sulphate, potassium bichromate.]

9. **Crystalline and Amorphous Bodies.**—Let us next see how these differences in the solubility of different bodies and of the same body at different temperatures can be made use of to separate mixtures into their constituents. First, look at the solution of copper sulphate which was left over from Expt. 8. If it has been left for a few hours you will find that it is now cold, and that the excess of copper sulphate, beyond what the cold water is able to dissolve, has separated out in beautiful dark blue *crystals*. These crystals have a definite geometrical shape, which in this case is rather complex. (See Fig. 7.) They have also another property which is characteristic of crystals—that of splitting readily in certain directions only. This property is called "cleavage," and is shown particularly well in the common mineral called calcspar.

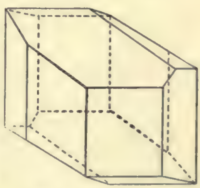

Fig. 7.—Crystal of copper sulphate.

Ex. 11.—*To show the difference between crystalline and amorphous solids.*—Take a piece of calcspar. Notice its shape, which is that of a rhombohedron—*i.e.* it has six sides, each of which is a rhomboid. Now take a hammer and break the piece of calcspar into several fragments. You will find that

each fragment will be a perfect rhombohedron, and that although the different individuals may differ in shape—some being broader and thicker than others—they all agree in having the *corresponding angles* equal. If you measure them you will find that the angle between any two adjacent faces is always either 74 deg. or 104 deg., no matter what the proportions of length, breadth, and thickness may be.

Take a piece of glass or rosin, break it and examine the fragments. You will find that their shape is quite irregular.

This experiment brings out the difference between **crystalline** and **amorphous** solids. Crystalline solids always show cleavage, though not always so distinctly as in the case of calcspar. Amorphous solids, on the other hand, do not show cleavage. When they are broken the faces of the fragments are usually curved, not flat as in the case of crystals; and the angles between the faces show no regularity, whereas in the case of crystals the faces are flat and the angles between them are constant for each particular substance.

The different behaviour of crystalline and amorphous substances may be compared to the difference between woven cloth and felt. Any woven material can be easily torn in two directions at right angles to each other, but it is almost impossible to tear it in any other direction. Felt, on the other hand, can be torn equally easily in all directions. The difference is due to difference of structure: in the woven material the fibres are arranged in two directions only—those of the "warp" and "woof." In felt they are arranged haphazard in all directions. The differences between crystalline and amorphous bodies are probably due to a similar cause—*i.e.* the particles of which crystals are built up are arranged in regular lines, while those of amorphous bodies are not.

10. Separation of a Mixture by Crystallisation.—Most substances when passing from the liquid or gaseous state to that of solid, whether in cooling after having been melted, or as the result of the cooling or evaporation of the liquid in which they have been dissolved, form crystals. Glass and rosin are among the exceptions to this rule. The form of the crystals is different as a rule, for each substance, though there are many cases of several substances crystallising in the same form. The following experiment will show how these differences may be

used to separate a mixture of two substances, both soluble in water.

Ex. 12.—*To separate alum from copper sulphate by crystallisation.*—Put into a small flask about 100 c.c. of water. Support the flask on a piece of wire gauze over the Bunsen flame. While the water is being heated take 100 gm. of copper sulphate and 50 gm. of alum, and grind them together in a mortar to a fine powder.

We have now a mixture of the two substances, and we shall next try to separate it by crystallisation. Add the powder in small portions at a time to the hot water, continuing to heat cautiously. When all is dissolved pour the clear liquid (filter it if it is not clear) into a porcelain basin, and leave it to cool slowly. Next day pour off the "mother liquor" and examine the crystals that are left. You will find two kinds, quite distinct from each other. There are white octahedral crystals of alum (Fig. 8) and blue prismatic crystals of copper sulphate. By picking out the white crystals and "recrystallising" them (that is, dissolving in a little boiling water and allowing crystals to form on cooling) we can get pure alum, and by the same process we can get pure copper sulphate from the blue crystals. In each case the impurity—copper sulphate in the first case, and alum in the second—remains in the mother liquor and by repeated recrystallisation can be completely got rid of.

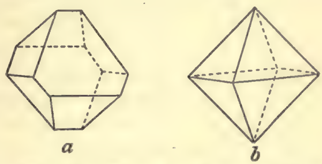

Fig. 8.—Crystals of alum: (*b*) is the ideal or perfect form; (*a*) is a common form produced by unequal growth of the faces.

11. Solubility in Liquids other than Water. — Other liquids may be used as *solvents* in the same way as water, though no other is so generally useful. Many substances which are insoluble in water dissolve readily in other liquids. For example, rosin does not dissolve in water, but dissolves readily in methylated spirit or alcohol.

Ex. 13.—*To further separate the constituents of gunpowder.*—Take some of the black powder which was left undissolved on treating gunpowder with water (Ex. 7). See that it is thoroughly dry, put it into a clean dry test-tube, and add to

it a few c.c. of *carbon disulphide*, a colourless, inflammable liquid having a very disagreeable odour. Shake the powder with the liquid for a little while, but do not heat, and take care not to bring any light near, as the vapour from the carbon disulphide takes fire very readily. Now filter through a *dry* filter paper and collect the filtrate in a clean dry basin. Leave both it and the filter paper for an hour or two, to allow the carbon disulphide to evaporate. You will find that the basin now contains small transparent yellow crystals which can be shown to be pure sulphur (heat one on a porcelain crucible lid, and notice that it burns with the characteristic flame and odour and leaves no residue). The black powder left on the paper is evidently an entirely different substance. Later on you will be able to identify it as charcoal or carbon. Notice that the crystals of sulphur are quite different in form (Fig. 9) from those of alum or copper sulphate.

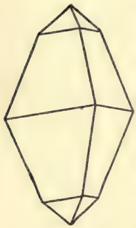

Fig. 9. Crystal of sulphur.

In Exs. 7 and 13 we have been able to separate gunpowder, by means of the processes of solution, filtration and crystallisation, into three components—sulphur, charcoal, and a white substance, soluble in water, called nitre. But how are we to be certain that each of these is not itself a mixture, capable by further treatment of being separated into different substances?

CHAPTER III

MIXTURES AND COMPOUNDS

12. There is no invariable rule by which we may always distinguish a pure substance from a mixture. Sometimes the distinction is difficult to make; but as a rule it is fairly easy. The following are some of the principal differences between mixtures and pure substances in the solid form :—

MIXTURES	PURE SUBSTANCES
The constituents can be distinguished by the eye with or without the aid of the microscope.	The appearance is *homogeneous* or uniform throughout, however minutely the substance be examined.
By solution and crystallisation crystals *of different kinds* can be got. (Ex. 12.)	Solution and crystallisation give crystals of one kind only. (Ex. 8.)
In many cases a particular solvent dissolves part of the mixture, leaving an insoluble residue. (Ex. 7.)	The substance dissolves uniformly—*i.e.* if it be treated with successive small equal portions of a solvent each of these will dissolve the same amount of substance. (Ex. 6.)
The properties are intermediate between those of the constituents.	The properties are (as a rule) quite different from those of either constituent.

When once a substance has been recognised as a pure or homogeneous substance it is usually easy to recognise it by its properties. The melting point is particularly useful in this respect. The boiling point, crystalline form, solubility, and specific gravity are also frequently used.

13. Mixtures of Liquids—Distillation.—Hitherto we have spoken only of mixtures of solids. In the case of liquids the separation of mixtures is more difficult, since in this case the mixture usually appears perfectly homogeneous. In many cases we may be able to convert the liquid into a solid by the application of cold. If it is a mixture one of the constituents will probably solidify before the rest, and in this way we may be able to effect a separation. This method is, however, not very convenient, though it will probably be used more generally in the future, as the appliances used for artificial cooling become more perfect. A more generally useful method depends on the fact that every pure liquid — unless it is decomposed by heat (Ex. 2)—has a definite boiling point.

Ex. 14.—*To find the Boiling Point of Alcohol.*—Put a few c.c. of absolute alcohol[1] into a dry[2] distilling flask, fitted with a thermometer, and connect it to a condenser kept cold by a stream of water (Fig. 10. For very small quantities the simpler apparatus shown in Fig. 31, p. 58, may be used to condense the vapour). Boil the alcohol and notice the temperature while it distils over into the receiver. If your thermometer is correct and the alcohol is fairly pure you will find that the mercury will rise quickly to about 78° C., and will remain steadily at that temperature until almost the whole of the liquid has distilled over. This temperature of 78° C. is the "boiling point" of alcohol (at the ordinary pressure of the atmosphere), and if the alcohol were perfectly pure the thermometer would remain absolutely steady at 78° until all the alcohol had distilled over. In the same way try the following liquids and determine the boiling point of each: — benzene, amyl acetate, chloroform. Take care to use a clean and *perfectly dry* flask in each case, and remember that the liquids and their vapours are very inflammable.

It will be found that each of these liquids has its own fixed temperature at which it distils. We shall next try the

[1] Methylated spirit will do almost as well provided it is without admixture of mineral oil. Permission to buy this can be obtained from the excise authorities.

[2] The flask is dried by warming it over a flame, and then blowing air from a bellows (not from the lungs) through it by means of a glass tube reaching nearly to the bottom of the flask. The process takes less time if the flask be first washed out with a few drops of methylated spirit.

effect of heat on a mixture of alcohol (boiling point 78°) and water (boiling point 100°).

Ex. 15.—*To separate a Mixture of Alcohol and Water.*—Mix together about 50 c.c. of alcohol and 30 c.c. of water. Place the mixture in a distilling flask and connect to a condenser, as in the last experiment. Now notice the behaviour of the thermometer when the mixture is boiled.

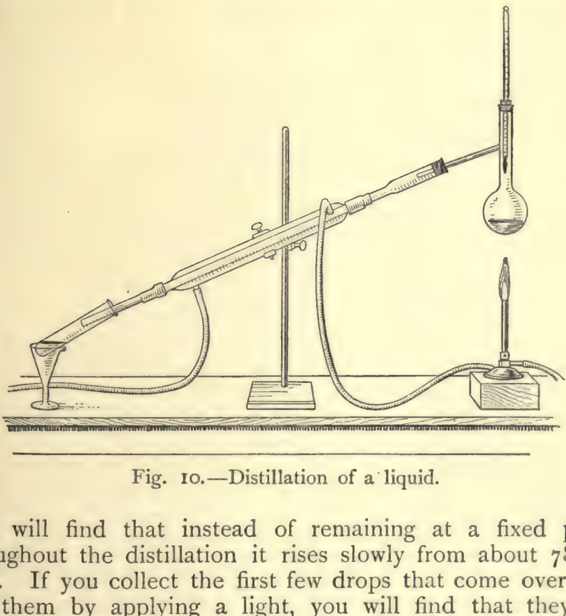

Fig. 10.—Distillation of a liquid.

You will find that instead of remaining at a fixed point throughout the distillation it rises slowly from about 78° to 100°. If you collect the first few drops that come over and test them by applying a light, you will find that they are tolerably pure alcohol; while the liquid left in the flask, after two-thirds of the mixture has been distilled, will be found to be nearly pure water.

We have thus effected a partial separation of the alcohol and water by the process of distillation. By repeating the process in a systematic manner we can generally get a portion of each liquid in a state of purity. This process is called "fractional distillation," and is the method most commonly used for the separation of liquids.

When an unknown liquid is found to have a constant boiling point, and therefore cannot be separated by fractional distillation into two or more components, it is usually safe to pronounce it a pure substance.

14. Mixtures of Gases.—The case of the separation of mixtures of gases is more difficult than those we have yet treated, and its consideration had better be left to a later stage of the student's progress.

15. Mixtures and Compounds.—From what has been said it will be evident that a substance may be a non-mixture or pure substance and yet not an element. For example, silver nitrate has all the characteristics of a pure substance—definite crystalline form, melting-point, solubility, density, etc. It cannot be separated by solution and crystallisation, nor by any mechanical means whatever into two different kinds of matter; yet we know that it *contains* at least two substances, for we have seen that when heated it splits up into metallic silver and a reddish gas. The silver is not merely mixed with the red gas—the union is of a far more intimate character, and is such that the original properties of both substances are entirely altered. In such a case the elements are said to be chemically combined, and the resulting substance is called a **chemical compound.** The mercuric sulphide prepared in Ex. 1, is another example of a chemical compound. It is not a mixture of mercury and sulphur but a chemical compound, and this is indicated in the name, which is made up of the names of the two elements with the endings "ic" and "ide," the exact meaning of which will be explained later.

So far, then, we may divide all known substances into (*a*) Pure substances, (*b*) Mixtures. The first class is subdivided into elements and compounds; the second may contain either or both.

The classification is shown in tabular form below:—

Non-Mixtures, or Pure Substances, or Chemical Individuals		**Mixtures**
ELEMENTS	COMPOUNDS (made up of two or more elements)	May contain two or more elements or two or more compounds or any number of both
Examples Silver Sulphur Mercury Carbon	*Examples* Mercuric sulphide Silver nitrate Mercuric oxide Nitre	*Example* Gunpowder (contains Nitre, Carbon, and Sulphur)

QUESTIONS AND EXAMPLES ON CHAPTERS I. II. AND III.

1. How would you prepare pure salt and pure sand from a mixture of the two?

2. At what temperature does a given weight of water dissolve equal weights of alum and of common salt? (Use the curves on p. 12.)

3. How could you prepare a solution containing 200 grammes of potassium chlorate to one litre of water without using a balance?

4. You are given a powder which consists of equal weights of potassium chlorate and potassium chloride mixed together. Suggest a means of obtaining a portion of each substance in the pure state.

5. What experiments would you make in order to decide whether a colourless liquid was pure water or not?

6. How could you obtain pure water from sea water? Sketch the apparatus you would use.

7. A white powder when thrown into water partly disappears and partly remains undissolved. What further experiments would you make in order to decide whether the original powder was a mixture or a pure substance?

8. A sample of powdered rosin is mixed with sand. How would you separate the two?

9. The melting point of a solid substance was found to be 80° C. On recrystallising it the first crystals which formed were found to melt at 85° C., while a second crop, got by evaporating the mother liquor, melted at 72° C. What inference would you draw as to the purity of the original substance?

10. 20 c.c. of a solution of a certain substance, saturated at 18° C., weighed 21·52 gm., and left on evaporation a solid residue which weighed 4·88 gm. Calculate (*a*) the specific gravity of the solution; (*b*) the solubility of the substance.

11. How would you obtain crystals of common salt from sea water?

12. At what temperature will 100 gm. of water just dissolve (*a*) 38 gm. of common salt; (*b*) 20 gm. of potassium chlorate?

13. How much water is required to just dissolve 10 gm. of alum (*a*) at 10° C.; (*b*) at 50° C.?

14. State some of the principal differences between mixtures and pure substances. What experiment would you make in order to decide whether oil of turpentine is a mixture or a pure substance?

CHAPTER IV

STUDY OF A TYPICAL EXAMPLE OF CHEMICAL CHANGE

16. Rusting of Iron.—The rusting of iron has already been mentioned as a good example of the changes that are classed as chemical, and it will be convenient to choose it as an example for further study. It is clear that iron rust is different from the iron from which it is produced. But in what does the difference consist? Does the iron combine with something (air or water, for example)? or does it lose some constituent by exposure to air? or is the change internal only —*i.e.* confined to some alteration or rearrangement of the particles of iron themselves? The answer to these questions will clearly be given by an experiment with the balance. If we take a weighed quantity of iron, allow it to rust, and then find the weight of rust produced, we shall find either (1) an increase of weight, (2) a decrease, or (3) no change. In the first case the iron must have combined with some new substance; in the second it must have given up some part of itself to the air; in the third it has (probably) done neither.

Ex. 16.—*To find whether there is any change in weight when iron rusts.*—Take a clean, dry porcelain basin or clock glass and a short piece of glass rod, weigh them together carefully and note the weight in your notebook. Now add three or four grammes of clean [1] iron filings, and weigh again. Moisten the filings with a few drops of pure water, stirring them up with the glass rod, cover the basin with paper to keep out dust, and allow the whole to stand for two or three days. Now warm the basin in an oven or on a sand-bath till the filings appear quite dry. Weigh, and note the weight. Heat again, and weigh a second time, to make sure that all the water has been

[1] The filings should be free from grease, and to ensure this they had better be washed beforehand with a little ether, and then allowed to stand until the ether has completely evaporated.

got rid of. (See Ex. 4.) You will find that the rusty filings weigh *more* than at first.

The last experiment shows that in rusting the iron combines with something. Our next question is—Where does the increase in the weight of the rusty iron come from? You can easily convince yourself by weighing the basin again that *its* weight has not changed. There remain only two possible sources of the increase—the water and the air. We have next to find out whether the increase comes from one or both of these.

Ex. 17.—*To find whether any air is used up when iron rusts.*—Take a tall, narrow, cylindrical glass jar (a test-tube will do very well on a small scale), put two or three grammes of clean iron filings into the bottom, add a drop or two of water, and turn the jar round and round so that the lower part is coated with a paste of iron filings[1] and water. Now place the jar, mouth downwards, in a basin of water and put the whole in a warm place. In a few hours you will find that the water has begun to rise in the jar, showing that some of the air has been absorbed. Mark the height to which the water has risen by gumming a strip of paper on to the glass, leave the apparatus for another day, and notice whether the water has risen further.

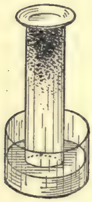

Fig. 11.

If it has, mark the level of the water again, and repeat your observations until the level of the water remains steady. Now find the cubical contents of the jar and the volume of air that has disappeared, by the following method:—

First pour water into the basin till the level of the water is the same outside and inside the jar. (What is the reason for doing this?) Now close the mouth of the jar by a tight-fitting glass plate, or by the thumb if a test-tube has been used. Remove the jar and pour the water into a graduated cylinder; its volume, of course, gives that of the air which has disappeared. Fill the jar completely and measure the water: this gives the cubical contents of the jar, and therefore the volume of air originally taken. Note the results for future use.

It is clear from this experiment that the iron does take

[1] After the experiment is over the rusted filings can be easily removed by a little strong hydrochloric acid.

something from the air, though we have not proved that the increase in weight is due to this alone. It is worth while to repeat this experiment in a different form.

Ex. 18.—Take a flask of not less than 300 c.c. capacity furnished with a tight-fitting india-rubber stopper. Put into the flask some iron filings and a few drops of water, as in the last experiment. Close the flask tightly, and weigh the whole apparatus. Allow the filings to rust, and then weigh again—no change in weight will be found. Now loosen the stopper: what happens? Weigh again. How do you account for the increase?

17. Indestructibility of Matter. — The last experiment illustrates a very important general principle—namely, that in any chemical action, if all the substances taking part be weighed before and after the action, the total weight of the new substances formed will be exactly the same as that of the original substances from which they were got. In this case, for example, the sum of the weights of the iron, water, and air with which we began is exactly the same as the sum of the weights of iron rust, water, and air left after the experiment. The principle may be expressed more shortly by the statement that **matter is indestructible.**

Of course this principle is not *proved* by the experiment you have just made, but merely illustrated. Such a general principle or "law" can only be proved by the united result of hundreds of different experiments all leading to the same conclusion. In this case not merely hundreds, but hundreds of thousands of experiments have been made, and in every case the law of the indestructibility of matter is found to hold good.

18. Does the Air, as a whole, combine with the Iron?—Having shown that the increase in weight of the rusted iron is due, at least in part, to its combination with something that is present in the air, we will next proceed to find out whether the air as a whole takes part in the change, or whether, as seems probable from the result of Ex. 17, only a portion of it is active. In Ex. 17 we found that only about 21 per cent. of the air (by volume) disappeared. But the action may have stopped because all the iron was used up. A simple experiment will enable us to say whether this was the case or not.

Ex. 19.—Repeat Ex. 17, marking the level of the water as before when it has become constant. Now lift the jar from the water, insert a glass tube nearly to the bottom, and suck out the air so that it may be replaced by fresh air; then re-invert the jar over water. You will find that the water will again rise slowly till 21 per cent. of the air has disappeared, and that then the action will cease.

The last experiment shows clearly that only about one-fifth of the air by volume is capable of acting upon the iron. So far as we have gone, then, it appears that when iron rusts the change is due to the combination of the iron with a gas which forms about 21 per cent. by volume of the air. But in all our experiments water as well as air has been present.

Another question now suggests itself—

19. Is the Presence of Water necessary for the rusting of Iron, or is Air alone required?—To answer this we must try whether rusting takes place when iron is exposed to the action of air alone, without the presence of moisture.

Ex. 20.—Put some bright "French nails" into a wide-mouthed, stoppered glass bottle, which should have been previously warmed before a fire to make sure that it is quite dry. Grease the stopper slightly with vaseline and insert it tightly. You will find that no rusting takes place even when the iron is left for months.

It appears, then, that water must be present in order that rusting may take place. It seems practically certain, from the result of Ex. 17, that the presence of air is also necessary. Yet it is worth while to make a special experiment to make this point quite clear.

Ex. 21. *To find out whether iron rusts in water free from air.*—Put some bright iron nails into a round-bottomed flask along with sufficient distilled water to nearly fill the flask.

Support the flask on wire gauze, or a sand-bath over a burner, and boil the water for at least a quarter of an hour. (This has the effect of expelling any air that may have been dissolved in the water.) Remove the flask, and *at once* (before the water ceases to boil) insert a tight-fitting india-rubber stopper. Now place the flask with its mouth under water in a basin, so that on cooling, even if the stopper should not be perfectly tight,

no air, but only a little water, can enter. You will find that the iron will remain quite bright.

It appears from these experiments that both air and water are necessary for the rusting of iron. To make a complete investigation of the action would involve experiments too difficult for a beginner, and we shall leave it at this point, and go on in our next chapter to a further study of the atmosphere.

CHAPTER V

THE ATMOSPHERE

20. Action of burning Phosphorus on the Air. — We have seen that only about one-fifth of the air by volume is capable of acting upon iron and combining with it to form iron rust. If we test the remaining inactive air left over from Ex. 17 or 19 by lowering into the jar a lighted taper [1] attached to a wire, we shall find that the flame is at once extinguished. It seems, then, that the same constituent of the air which combines with iron is also concerned in the action that occurs in the burning of a candle. That this is the case we shall find later on. Meanwhile it will be easier to study the combustion of phosphorus, because in this case the action is simpler than in the case of the candle, only one new substance being produced, and this a *solid*, and therefore easily separated from the residue of inactive air. (In the case of the candle the products of combustion are gaseous and remain mixed with the air.)

Ex. 22.—Cut off *under water* a piece of phosphorus about the size of a pea, take it up with a pair of crucible tongs and place it on blotting-paper to drain. (Phosphorus is so inflammable that the heat of the hand is sufficient to set fire to it. It must therefore be kept under water and never touched with the naked fingers.) Now with the (previously dried) tongs place the phosphorus on a piece of plate glass, set fire to it by touching it with a hot wire, and immediately cover it with a dry glass bell-jar having a ground rim which has been greased so as to fit closely to the glass plate. The phosphorus burns brightly and the jar becomes filled with dense white fumes. Leave the whole to become perfectly cold, and then remove the bell-jar. You will find that the fumes have settled on the glass plate in the form of a white snow-like powder — phosphoric oxide. Notice also what

[1] An ordinary wax match is most convenient.

happens when the white powder is exposed for a few minutes to the air.

We will next repeat the last experiment in such a way that we can observe any change that may occur in the volume of the air employed.

Ex. 23.—Arrange an apparatus as shown in Fig. 12. The bell-jar *B* stands in a basin of water in the centre of which a small bottle (also filled with water) serves as a support for a porcelain crucible containing the piece of phosphorus. *R* is a glass rod previously rubbed with vaseline or glycerine so that it slides readily, yet air-tight, through the hole in the rubber stopper *S*. When all is ready the level of the water in *B* is carefully marked. The stopper is next taken out and the point of *R* is heated in the flame of a lamp. The stopper is now put in tightly and *R* is pushed down until it touches the phosphorus, which takes fire and burns brightly. Notice exactly what takes place. At first the level of the water falls. How do you account for this? Afterwards the water rises, and this is what we should expect to find if the phosphorus, like the iron, combines with something from the air. To find how much air has disappeared, allow the apparatus to get quite cold (why is this necessary?) and then proceed as in Ex. 17. You will find that, as before, about 21 per cent. by volume of the air has disappeared. Test the remaining gas with a lighted taper, after pouring water into the basin until the water stands at the same level outside and inside the bell-jar. (Why is this necessary?) Make sure also that some phosphorus remains unburned by touching it with a heated wire or glass rod.

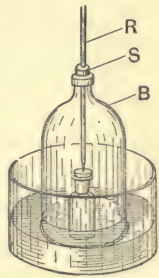

Fig. 12.—Experiment to find out how much air is used up when phosphorus burns.

It is easy to show that in the case of the phosphorus, as in that of the iron rust, the new compound weighs more than the original solid from which it was formed.

Ex. 24.—Take a dry round-bottomed flask of about 300 c.c. capacity fitted with a good india-rubber stopper. Put into it a small piece of phosphorus previously dried on blotting-paper. (Observe the precautions mentioned in Ex. 22.) Press in the stopper very tightly and then carefully weigh the flask.

Now dip the bottom of the flask for a moment into warm water. The phosphorus will take fire, and as soon as it does so the flask should be covered with a cloth and held at arm's length in case it should burst. It is well also to turn the flask round several times so that the melted phosphorus may be spread over the glass. When the action is over allow the flask to get quite cold, then dry it and weigh again. Since nothing has been allowed to enter or escape we shall find that the weight is unaltered. Now loosen the stopper. Air will rush in to take the place of that which has combined with the phosphorus, and on replacing the stopper and weighing a third time you will find a distinct increase.

This experiment shows once more (*a*) that matter is indestructible; (*b*) that when a substance burns in the air, the new body formed weighs more than the original body. This increase, of course, must come from the air. In this case, for example, if the white phosphoric oxide weighs 0·1 gm. more than the phosphorus, it is because it has combined with 0·1 gm. of another element from the air.

These experiments show clearly that *the air is a mixture or compound of at least two gases, one of which is able to combine with iron, phosphorus, and other bodies, while the other is comparatively inactive.*

21. Separation of the active Constituent from Air.—The separation of the active constituent of the air from the inactive is somewhat difficult. In principle, the simplest method is to cool the air down sufficiently to liquefy it, and then to separate the two constituents by the process of fractional distillation. (Ex. 15.) In practice, however, this method requires elaborate and costly apparatus, and it will be better to choose a method which is easily carried out on a small scale. The most obvious plan seems to be to try to decompose the compound formed by iron, phosphorus, or some other element in combining with air. The compounds with iron and phosphorus are not suitable, for they are very difficult to break up again; but several other metals form compounds, which can be broken up and thus used to set free the active constituent.

Ex. 25.—Fit up a round-bottomed flask as in Fig. 13. The long tube ends just below the cork, while the short one reaches

within an inch of the bottom of the flask. Put about 50 c.c. of mercury into the flask, and support it on a retort stand close above a Bunsen burner. The short tube should end just above the surface of the mercury, which will therefore be heated in a constant current of air. Adjust the flame so that the mercury shall be heated just to its boiling point, and leave the apparatus to stand for a day or two. You will find that black specks will begin to form on the surface of the metal after it has been heated for an hour or two, and that these will gradually increase in size and number as the heating is continued. When sufficient of this new substance has been formed, which should be in two days at most,[1] remove the burner and allow the apparatus to cool, pour out the mercury into a basin and collect as much of the now dark red powder as you can. Put it into a very small test-tube made of "hard" or infusible glass, connect this by a short piece of thick-walled rubber tubing to a glass leading tube of the shape shown in Fig. 14, and support the whole on a retort stand, so that the end of the leading tube dips under the water of the "pneumatic trough" (a pudding-dish will do very well for this),[2] as shown in the figure. A wide test-tube is to be completely filled with water and inverted over the mouth of the leading tube, so that any gas which escapes will pass up into it. Now heat the tube rather strongly with a Bunsen flame. Bubbles of gas will escape and collect in the inverted test-tube. When no more

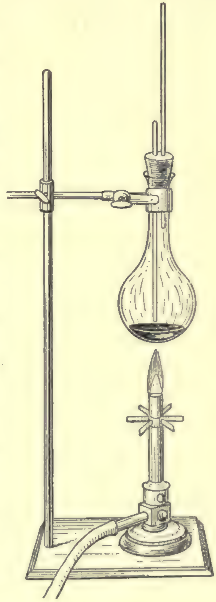

Fig. 13. — Heating mercury in a current of air to convert it into oxide.

[1] In an actual experiment 1·36 gm. of the oxide (sufficient to give 50 c.c. of oxygen) was formed in 28 hours.

[2] Perhaps the most convenient pneumatic troughs for school use are small rectangular tanks of enamelled sheet iron, measuring 9 in. long by 4 in. wide and 3 in. deep. Suitable gas jars are 5 or 6 in. high and 1½ in. diameter.

gas escapes close the tube tightly with the thumb of the left hand, remove it from the water, turn it mouth upwards, and quickly insert a glowing splinter of wood or piece of string. The splinter bursts into flame. Notice that the dark red powder has entirely disappeared, and the small test-tube now contains only mercury.

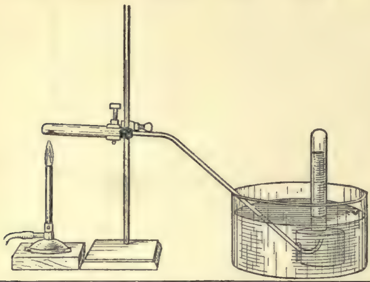

Fig. 14.—Preparation of oxygen by heating mercuric oxide.

In this experiment we have separated the active gas from the air by first causing it at a moderate temperature to combine with mercury to form the red powder, mercuric oxide, and then breaking up this compound by intense heat into its elements—mercury and *oxygen*, as we shall henceforth call the active constituent of the air. This method of preparing oxygen is not very convenient, even when the oxide of mercury is prepared (as it can be) by an easier method than that which we have used. But it is of great interest, because it was by means of this experiment (in a slightly different form) that the great French chemist, Lavoisier, was able for the first time to give a correct explanation of the chemical changes that occur in combustion.

22. **Action of Heat on Potassium Chlorate.**—In order to prepare a larger quantity of the gas we shall make use of a white crystalline substance called potassium chlorate, which has the advantage over mercuric oxide of being cheaper, of containing a much larger proportion of oxygen, and of giving up its oxygen at a much lower temperature.

Ex. 26.—Heat a few crystals of potassium chlorate in a clean dry test-tube. Notice that the crystals first crackle, then melt, and that then, at a higher temperature, the liquid seems to boil. It does not really boil—if we try to distil it we shall get nothing but gas in the receiver—so it is more correct to say that the liquid "effervesces," that is, it gives off small bubbles of gas. That this gas is oxygen is easily shown by

testing with a glowing splinter. Repeat the experiment, using a weighed quantity of the chlorate (about one gramme) heated in a small porcelain crucible with a cover. The crucible (with its cover) is first weighed empty, then the approximate quantity of powdered potassium chlorate is put in, and the weight again found. The crucible is now supported on a triangle made of iron wire covered with pipe stems, and resting on the ring of a retort stand, and is strongly heated by a Bunsen flame until effervescence has ceased. It is then allowed to cool, and weighed. To make sure that all the oxygen has been driven off the crucible is again strongly heated for five minutes, allowed to cool, and weighed a fifth time. If the result agrees with the fourth weighing we know that the action is complete. If not, the crucible must be heated and weighed again, until two successive weighings give the same result.

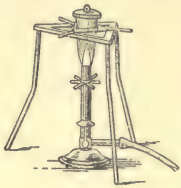

Fig. 15.

Here is an example of how to record your results :—

Weight of crucible + lid . . .	5·638 gm.
Do. do. do. + chlorate .	6·582 ,,
∴ Weight of potassium chlorate taken .	0·944 ,,
Weight after heating 1st time . .	6·212 ,,
Do. 2nd ,, . .	6·208 ,,
Do. 3rd ,, . .	6·208 ,,

∴ Loss in weight (= weight of oxygen given off?) = 6·582 - 6·208 = 0·374 gm.

Examine the white residue in the crucible. It is called potassium chloride, and differs from potassium chlorate in melting-point, solubility, relative density, etc., as well as in containing no oxygen.

Calculate from your result the percentage of oxygen contained in potassium chlorate, assuming (what we have not yet proved) that nothing but oxygen is given off on heating. If you have performed the experiment carefully your result should be approximately 39·2 per cent.

Since the oxygen evidently must have existed in chemical

combination in the potassium chlorate, it is clear that this substance must be another example of a chemical compound, and the last experiment brings out incidentally what we shall find to be a characteristic property of all chemical compounds —namely, that **chemical compounds contain their elements in fixed and definite proportions by weight.**

Potassium chlorate can be prepared by several very different methods; but no matter how prepared, it invariably contains 39·2 per cent. by weight of oxygen, neither more nor less.

Mercuric oxide contains a much smaller proportion of oxygen, as you can easily prove by repeating Ex. 26 with it. But in this case a crucible must not be used, since the mercury would be "volatilised"—*i.e.* driven off as gas. By heating a weighed quantity of *pure* mercuric oxide[1] in a test-tube of hard glass held horizontally, the mercury will condense in the cold part of the tube, and can be weighed after the experiment, when we shall find that for every one gramme of mercuric oxide taken we shall get ·926 gm. of mercury and only ·074 gm. of oxygen.

23. Preparation of Oxygen.—When heated alone, potassium chlorate requires a rather high temperature to "decompose" it, but when mixed with even a very little of a black powder called manganese dioxide (a compound of the metal manganese with oxygen) it gives up its oxygen at a very much lower temperature, and this is the method by which oxygen is usually prepared in the laboratory. The action of the manganese dioxide is not easy to explain. It is itself not altered, as can easily be proved by weighing it beforehand and again after the experiment. (It can be readily separated from the potassium chloride, for it is insoluble in water, while potassium chloride is readily soluble, and, accordingly, we have only to proceed as in Ex. 7 to separate the two.) It will be convenient to prepare several litres of oxygen for further experiments.

Ex. 27.—Fit up the apparatus shown in Fig. 16. *A* is an ordinary large test-tube furnished with a tight-fitting india-rubber stopper, through which passes a short piece of glass tubing *B*, bent at right angles, which passes through the doubly-bored rubber stopper of the gas-holder *C*, ending

[1] The oxide made by heating mercury in the air always contains unchanged mercury in minute globules which are difficult to get rid of completely.

just below the stopper. A second tube *D*, also bent at right angles, passes from the bottom of *C* and by a long rubber tube *H* to the reservoir *F*, which is intended to hold the water expelled from *C* by the gas entering from *A*. Into *A* put about 15 or 20 gm. of potassium chlorate mixed with about one-fifth of its weight of manganese dioxide. (The mixture need not be intimate, and the potassium chlorate had better be in crystals, not in powder.) Now insert the stopper and make sure that the whole apparatus is air-tight by sucking at *F*. Fill *C* with water, put its stopper in tightly, see that the clip *E* is open and then heat the mixture in *A* carefully, beginning at the end next *B*. The oxygen will collect in *C*, driving the water over into *F*. When sufficient has been collected the tube *A* may be disconnected and *B* closed by a short piece of rubber tubing and a clip.

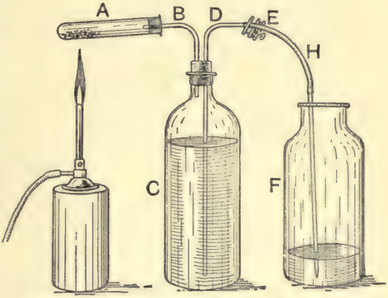

Fig. 16.—Preparation of oxygen from potassium chlorate.

We have now to prove that the gas which we have prepared by heating potassium chlorate is really the chemically active constituent of the atmosphere, and to find out what we can about its properties. We have seen that a taper or a splinter of wood burns very brilliantly in the gas, which is just what we should expect to find if it is this gas which is removed from the air by the iron in Ex. 17 and by the phosphorus in Ex. 22. Evidently, if we expose moist iron filings to oxygen *the whole* of the gas should be absorbed, and this can easily be shown to be the case.

Ex. 28.—Connect a leading tube *M* to the tube *B* of the reservoir containing the oxygen, and place the end of this under a test-tube (*L* in the Fig.) standing over water in the pneumatic trough. Now raise the reservoir *F* and open the clip at *B*. The water from *F* will flow into *C* and some oxygen will be expelled and will pass into *L*. When *L* is

full close the clip at *B*. Now wrap a gram or so of clean iron filings in a little tissue paper and pass it under the water into *L*. Close the mouth of the tube tightly with the thumb, shake vigorously so as to spread the iron filings over the interior of the tube, and then leave it to stand, mouth downwards, in a saucer full of water. The water will gradually rise and ultimately will fill the tube completely.

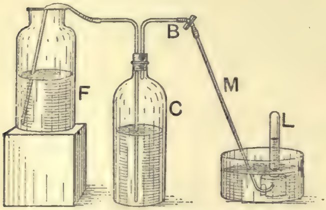

Fig. 17.—Filling a test-tube with oxygen from the reservoir.

A similar experiment might be carried out with phosphorus; but there is danger of the phosphorus catching fire, and it will be better not to attempt the experiment.

24. Can Air be made by mixing Oxygen with the Gas left over when Iron rusts in Air?—It now only remains to show that we can get ordinary air from its constituents, oxygen and the inactive gas left after the absorption of the oxygen by iron or phosphorus, by mixing them in the proper proportions.

Ex. 29.—Repeat Ex. 17, or Ex. 22, but after the absorption of the oxygen pass into the jar sufficient oxygen from the gas-holder to replace the gas that has disappeared. Wait a few minutes to allow the gases to become thoroughly mixed, noticing meanwhile whether you can detect any evolution of heat or other sign of chemical action. Then test the gas by introducing a lighted taper. You will find that the taper will burn exactly as in ordinary air.

25. Summary of what has been proved.—In this and the preceding Chapter we have shown:

(1) That when iron rusts or phosphorus burns in the air, one-fifth of the air by volume combines chemically with the iron or phosphorus, the other four-fifths remaining inactive.

(2) That the chemically active constituent, oxygen, may

be separated from the other (nitrogen) and obtained in the pure state by means of mercury.

(3) That matter is indestructible (illustrated). For example, when phosphorus burns, the gain in weight of the phosphorus is exactly equal to the loss in weight of the air.

(4) That chemical compounds contain their elements in fixed and unvarying proportions by weight.

QUESTIONS AND EXAMPLES ON CHAPTERS IV. AND V.

1. When iron is strongly heated black scales form on its surface. Suggest an experiment by which you could find out whether this change is due to combination with oxygen.

2. What inference can you draw from the result of Ex. 29 as to whether air is a mixture or a chemical compound of oxygen and nitrogen?

3. What addition can we now make to the table of differences between mixtures and compounds given on p. 17?

4. What is the difference between melting and solution? Does a lump of sugar melt or dissolve when put into water?

5. Describe exactly, with sketches of the apparatus you would use, how you could prepare oxygen gas from the air.

6. What weight of potassium chlorate would be required to give 15·68 grammes of oxygen?

7. Describe exactly what happens when mercuric oxide is strongly heated. Which of the changes that take place do you consider to be chemical changes, and which physical? Give reasons for your answer.

8. Describe, with sketches of the apparatus you would use, two different methods of depriving air of its oxygen and finding the proportion of the other gas which it contains.

9. Describe fully an experiment to show that chemical compounds have a constant composition.

10. 10 grammes of potassium chlorate are mixed with 2 gm. of manganese dioxide and heated in a test-tube till no more gas is evolved. What weight of residue will be left?

11. If the contents of the tube (ques. 10) be dissolved in water, filtered, and evaporated to dryness, what weight of potassium chloride will be left?

12. What weight of oxygen gas is given off on heating 20 gm. of potassium chlorate?

13. What weight of mercuric oxide must we heat in order to obtain 1·48 gm. of oxygen?

14. What is meant by the statement that matter is indestructible? Describe an experiment to illustrate the truth of the statement.

15. Describe an experiment to show that when phosphorus burns in the air, the new substance formed weighs more than the original phosphorus.

CHAPTER VI

OXYGEN AND NITROGEN

26. Other properties of Oxygen.—The most important *chemical* property of oxygen is its tendency to combine with most of the other elements to form compounds called **oxides.** In some cases this combination goes on at the ordinary temperature—*e.g.* when iron rusts. But in most cases it is necessary to heat the substance before combination begins—for example, a taper or piece of wood remains quite unchanged in air or oxygen until it is "lighted"—that is, until a part of it is heated to the temperature at which it is able to combine with oxygen. When once the combination has been begun, the heat produced by the chemical action is usually more than sufficient to keep up the necessary temperature, and, as a rule, the substance becomes so hot that light is emitted. Whether the action is slow or rapid, however, heat is always produced. Even in the rusting of iron it can easily be shown that this is the case. We have only to repeat Ex. 16, using a large quantity of iron filings in a bottle surrounded by cotton wool, to find that a thermometer placed in the moistened filings will show a rise of temperature amounting to several degrees. In this case the heat is evolved gradually, and its effects are consequently imperceptible without special appliances. But iron can also be made to burn in the ordinary sense of the word, and in this case the heat is evolved rapidly and is evident to the senses.

Ex. 30.—Twist some thin iron wire (florist's wire will do very well) round a pencil so as to make a long spiral. Tie to one end of the spiral a small piece of waxed thread; this will serve to begin the combustion of the iron. Now fill a jar with oxygen as in Ex. 28, cover the mouth with a glass plate, and place the jar mouth upwards. Remove the cover for a moment and slip in a circular piece of filter paper, which should be large enough to cover the bottom

of the jar. Add enough water to wet the paper thoroughly. Now light the waxed thread at the end of the spiral of wire and plunge it into the jar of oxygen. The iron will burn brilliantly, and small drops of molten oxide of iron will fall from it on to the wet paper at the bottom. (Without this they would melt their way into the glass and crack it.) If the wire be weighed before the experiment, and the unburnt portion with the drops of oxide (of course carefully dried) be weighed again after it, we shall find that, as in the case of Ex. 16, there has been an increase in weight. Compare the properties of the oxide obtained with those of the rust formed in Ex. 16. Are the two substances identical? (Test both with a magnet.)

27. Oxides of Metals and of Non-Metals. — The oxide formed in the last experiment is a solid substance, and this is generally the case with the oxides of metals. Many elements, however, form oxides which are gaseous at the ordinary temperature.

Fig. 18.

Ex. 31.—Fill several jars with oxygen and try to burn in them (separately) the following elements:—magnesium, copper, zinc (in thin foil or ribbon); charcoal, sulphur, phosphorus. In the last three cases a small piece of the substance, about the size of a pea, is placed in a "deflagrating spoon"[1] (Fig. 18), ignited by holding one corner in the Bunsen flame, or in the case of phosphorus by touching it with a hot wire, and then plunged into the jar of oxygen. Which burn and which do not? Describe the oxides produced. Try the effect of each on a little neutral litmus solution and note the effect.

[1] Satisfactory deflagrating spoons may be made from pieces of stout iron or aluminium wire about 40 cm. long. The wire is fixed vertically by its lower end in a vice and is then bent over and wound round itself into a flat spiral of about 2 cm. in diameter. The straight part of the wire is then bent into the vertical position to form the handle, and the spiral is hollowed into a little bowl by pushing down its centre. The handle is passed through a piece of cardboard or sheet metal held between two corks. In burning sulphur and phosphorus the bowl may be protected by covering it with a little circle of asbestos paper, previously heated for a few seconds in the Bunsen flame in order to free it from combustible matter.

28. Density of Oxygen.—We shall next make an experiment to find whether a given volume of oxygen weighs more or less than the same volume of air.

Ex. 32.—Select a round-bottomed flask of about 250 c.c. capacity, and fitted with a perforated rubber stopper through which a bent tube, which can be closed at will by a stopcock or clip, passes to the bottom of the flask. Suspend it to one arm of the balance by a piece of thin copper or aluminium wire and carefully weigh it. Note the temperature and pressure at the time, and take care that the clip is open and that the air in the flask has not been warmed by handling. Now connect the tube to the oxygen reservoir (Fig. 19), loosen the stopper, and send a *brisk* current of oxygen into the flask until the gas escaping round the stopper quickly rekindles a glowing splinter of wood. Continue the current for another minute, then tighten the stopper, close the clip, and again weigh the flask, which is now full of oxygen. If a good air-pump is available, the flask should next be exhausted and weighed empty.[1] Lastly, the capacity of the flask is determined, as in Ex. 17. By subtracting the weight of the empty flask from (*a*) the weight of the flask full of air,

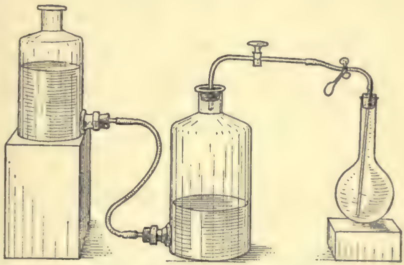

Fig. 19.—Filling a flask with oxygen by displacement.

[1] The "Geryk" air pump, made by the Pulsometer Engineering Co., Reading, is specially recommended as giving excellent results and being very easily kept in order. Where there is a supply of water at sufficient pressure the glass jet pumps sold at about 2/- answer admirably. If neither this nor an ordinary air-pump is available, the weight of a given volume of air may be found by boiling a small quantity of water in the flask so as to expel all air, and closing the clip at the same moment that the flask is removed from the source of heat. It is then allowed to cool and weighed. The clip is then opened and the increase in weight caused by the air which rushes in is determined. The volume of water left must, of course, be deducted from the capacity of the flask in estimating the volume of the air.

and (*b*) the weight of the flask full of oxygen, we can find the relative density of the two gases. It will be found that oxygen is about 1·12 times as heavy as air.

Since all gases expand and contract alike with alterations of temperature and pressure, this result will be the same whatever the temperature and pressure of the air may be (always provided, of course, that they do not change during the experiment). But the actual weight of a litre of air or oxygen will vary on different days, being more when the temperature is low and the pressure high, and less under the opposite conditions. In all experiments on gases it is therefore usual to note the temperature and pressure of the gas at the same time that its volume is read off, and to calculate what the volume would have been had the temperature been 0° C., and the pressure equal to that of a column of mercury 760 mm. high. This temperature and pressure have been fixed arbitrarily as the standard or *normal*, and when the volume of a gas is given as so many c.c. at "N.T.P," it means that this would be the volume were the gas measured at 0° C. and 760 mm. pressure.

29. Properties of the inactive Constituent of the Air.—We have seen that in all the chemical changes in which air takes part (so far as we have studied them), only one constituent, that which we have now learned to call oxygen, is really active. It is now time to give some attention to the inactive gas which, as we have seen, forms about four-fifths by volume of the air. Until quite recently this was believed to consist of a single gas, to which the name **nitrogen** was given, for a reason that will be more readily understood later on.

It is now known that the nitrogen is mixed with a small proportion (about 1 % of its volume) of another gas called *argon*, which is distinguished from it by possessing a higher relative density, but in other respects resembles nitrogen so closely as to render its detection and separation very difficult.

We have already found (Ex. 23) that nitrogen will not allow ordinary combustibles to burn in it, even burning phosphorus being extinguished when plunged into a jar of the gas. In other words, nitrogen does not readily combine with other elements —it is chemically a very inert substance. Indeed, it is chiefly by negative tests—by the things it will *not* do—that it is distinguished from other gases. Its physical properties may also be made use of for this purpose. Since we found that oxygen is heavier than air, bulk for bulk, we should expect to find that

nitrogen is lighter; and this is actually the case. Its relative density may be determined in exactly the same way as that of oxygen. The only novelty in the experiment will be in the method of filling the flask with nitrogen. For this purpose we may use the apparatus shown in Fig. 20, which will be seen to be a modification of that already used in Ex. 32. The air in the bottle *C* is deprived of its oxygen by a stick of phosphorus (*P* in the figure) which is scraped clean (under water, of course), and then tied by thread to the tube which passes through the cork of *C*. The apparatus is left to stand, the stopcock *B* being closed. The phosphorus gradually combines with the oxygen, forming white fumes of oxide, and water is drawn over from *F*.[1] When no more water passes over *F* may be raised, and the stopcock *B* opened so as to drive the nitrogen over into the flask *O*. The rest of the experiment is carried out exactly as in the case of oxygen.[2] (Why is the flask *O* to be held mouth downwards?)

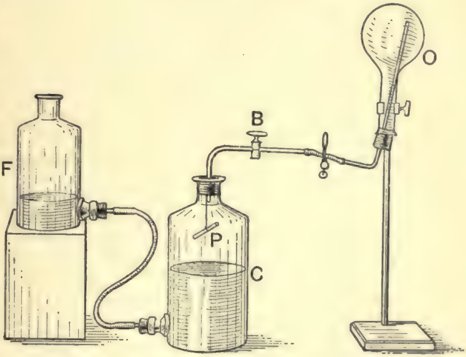

Fig. 20.—Filling a flask with nitrogen.

The following table gives the weight of one litre of oxygen, nitrogen, and air respectively at N.T.P., as found from more accurate experiments:

	Wt. of 1 litre at N.T.P.	Rel. density (air = 1)
Oxygen	1·44 gm.	1·12
Nitrogen . . .	1·26 ,,	0·98
Air	1·29 ,,	1·00

[1] Instead of the phosphorus, a muslin bag containing moistened iron filings and suspended from the cork which closes the bottle *C* may be used.

[2] *Note for the teacher.*—To save time, the determination of the relative density of air, oxygen, and nitrogen may be carried out simultaneously, one-third of the class being told off for each experiment, and the results afterwards collected and discussed at the blackboard.

30. Is Air a Mixture or a Compound?—The preceding experiments have shown that air is made up of 21 % by volume of oxygen and 79 % by volume of nitrogen (and argon). We have next to ask ourselves whether the two gases are combined or merely mixed. We have already seen (Ex. 29) that ordinary air is produced when the two gases are mixed in the correct proportion, and that *no change of temperature or other sign of chemical action* can be observed. It has also been mentioned that liquid air has not a constant boiling-point, but can be separated by fractional distillation, the more volatile nitrogen distilling off first, and leaving part of the oxygen behind in a nearly pure state. Both these circumstances point clearly to the fact that air is a mixture and not a compound. Again, the physical properties of a mixture can always be calculated if we know those of the substances which make it up, and the proportions in which they are present; but this cannot be done with compounds—the properties of a compound are usually quite different from those of its elements. Let us apply this principle to the case of air. If it be a mixture, we should be able to calculate the weight of a litre of air from that of its constituents. One litre of air is made up of ·79 litre of nitrogen and ·21 litre of oxygen. Now, since one litre of nitrogen at N.T.P. weighs 1·26 gm., ·79 litre will weigh $1{\cdot}26 \times {\cdot}79 = {\cdot}995$ gm.; and ·21 litre of oxygen at N.T.P. will weigh $1{\cdot}44 \times {\cdot}21 = {\cdot}302$ gm. Adding these two together we find that the weight of one litre of air at N.T.P., assuming it to be a mixture, should be ${\cdot}995 + {\cdot}302 = 1{\cdot}297$ gm., and this is almost exactly the number found by experiment. We may therefore take it as certain that the oxygen and nitrogen in air are merely mixed and not chemically combined. Indeed, there is only one circumstance that seems to point to the opposite conclusion—the fact that air has a very nearly constant composition. Constancy of composition is, as we have seen (p. 34), a characteristic of chemical compounds. But in the case of air the constancy is only approximate—slight differences are found at different times and in different places—and it is easily accounted for by the constant circulation kept up by winds and air-currents.

31. Solubility of Oxygen and Nitrogen. — We have seen that most solids are more or less soluble in water. Is this

also the case with gases? A simple experiment will answer the question in the cases of oxygen and nitrogen.

Ex. 33.—Boil some water for at least half-an-hour, and put it while still very hot into a bottle, which must be filled to the brim. Close the bottle tightly with an india-rubber stopper, taking care to leave no air between the stopper and the water. Allow the water to cool. Now take a glass tube of uniform diameter, not less than 50 cm. long and 1 cm. bore, and closed at one end. If it is graduated in c.c. so much the better; but this is not necessary. Fit it with an india-rubber stopper through which passes a short piece of narrow bore tubing fitted with a rubber tube and a clip at one end (see Fig. 21). Now fill the long tube to about three-fourths of its length with the water which has been boiled and allowed to cool. Mark the height of the water and note its temperature (which should be the same as that of the room). Now fill the upper part of the tube with oxygen from the gas-holder, quickly insert the stopper, and put on the clip as close as possible to the glass. We have now a certain volume of water enclosed with a certain volume of oxygen at the temperature and pressure of the room. Shake the tube violently for several minutes so as to bring every part of the water into contact with the gas. Now put the mouth of the rubber tube under some of the cold boiled water in a basin, holding the glass tube nearly horizontal, so that the pressure on the gas inside it may be the same as that of the atmosphere: squeeze out any air that may be in the rubber tube, and lastly open the clip. Water will now flow in to take the place of any gas that has been dissolved. Repeat the shaking and opening under water, to make sure that no more gas will dissolve, and lastly put the tube mouth upwards and mark the level of the water. The difference between this and the original level gives the volume of oxygen that has dissolved in the water.

Fig. 21.—Apparatus for determining the solubility of gases in water.

It will be found that at ordinary temperatures about 3 c.c. of oxygen dissolve in 100 c.c. of water, and that the amount is *greater* the lower the temperature of the water—exactly the opposite of what we found in the case of solids, which are, as a

rule, much more soluble in hot than in cold water. The experiment should be repeated[1] with nitrogen and air. It will be found that nitrogen is only about half as soluble as oxygen, and that the solubility of air, as we should expect, is between the two, but much nearer to that of nitrogen.

32. Summary.—In this chapter we have learned—

(1) That oxygen combines readily with many other elements, sometimes at the ordinary temperature (iron, phosphorus) —more often only when the action is started by heat.

(2) That in all such cases, whether the combination be slow or rapid, heat is evolved.

(3) That of the compounds (Oxides) formed some are solids and some gases; and that some (phosphorus and sulphur oxides) change the colour of neutral litmus solution from purple to red, while others have no action upon it, and one (magnesium oxide) slowly changes the colour to blue.

(4) That oxygen is denser and more soluble in water than air, while nitrogen is less dense and less soluble.

(5) That air is a mechanical mixture and not a chemical compound.

QUESTIONS AND EXAMPLES ON CHAPTER VI.

1. What is an oxide? Give two examples.

2. Describe a simple experiment to prove that air is a mixture and not a chemical compound.

3. The relative density of coal gas is ·45 (air = 1). Calculate the weight of 100 litres of coal gas at N.T.P.

4. Describe exactly what happens when a piece of sulphur is lighted and then placed in a jar of oxygen.

5. Describe, with a sketch of the apparatus you would use, how to determine the relative density of coal gas.

6. How could you show that heat is given out when iron rusts? Why is it that under ordinary circumstances this heat is not noticed?

7. What is the effect on neutral litmus solution of the oxide produced by burning (*a*) phosphorus, (*b*) iron, (*c*) magnesium in oxygen?

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[1] Or carried on concurrently by different pupils.

8. A mixture of equal volumes of oxygen and nitrogen is shaken up with a large volume of cold distilled water. What happens? What difference would there be in the composition of the mixture after the experiment? How would you show this difference by experiment?

9. If the water used in the last experiment (ques. 8) were boiled and the gas which had been dissolved in it were collected, what difference should we find in its composition as compared with that of the original mixture of oxygen and nitrogen?

10. Calculate the weight at N.T.P. of one litre of a mixture of oxygen and nitrogen in equal volumes.

11. Explain fully the meaning of the expression "N.T.P." (Normal Temperature and Pressure.)

12. In what kind of weather has a litre of air the greatest weight?

CHAPTER VII

COMBUSTION, AND STUDY OF WATER

33. What Chemical Changes occur when a Candle burns? —We have seen that when phosphorus or iron burns in air or oxygen, the chemical action that occurs is a simple one, being merely the direct union of two elements—the phosphorus or iron on the one hand, and the oxygen on the other. Let us try next to find out something of what takes place when a candle burns.

Ex. 34.—Take a clean and perfectly dry bottle (see p. 18 for method of drying), which should be made of clear glass. Fasten a small piece of candle[1] to a piece of soft iron or copper wire. Light the candle and put it into the bottle, covering the mouth with a piece of cardboard if it is at all wide. Notice exactly what happens to the flame. Afterwards examine the sides of the bottle carefully (use a lens). What do you find?

Fig. 22.

Since we know that a candle will burn brilliantly in oxygen, but not at all in nitrogen, we may fairly assume that when it burns in air the action that takes place is like that which occurs when phosphorus burns—*i.e.* that the material of the candle is combining with the oxygen of the air to form a compound. The only *visible* product of the change is the coating of minute drops of liquid which you have seen on the sides of the bottle. But is this the *only* product? Another experiment will help us to answer the question.

Ex. 35.—Arrange the apparatus shown in the figure. *B* is a bell-jar containing air, and stands over water in the trough or basin *T*. *S* is a tight-fitting rubber stopper, through which passes air-tight a glass rod *R*, which is drawn out to a long fine

[1] The small candles sold at toy-shops for decorating Christmas trees are suitable for this and similar experiments.

point at its lower end. *A* is a piece of candle, to the wick of which is attached (by melting the wax) the cap of inflammable composition which has been removed from an ordinary wax match. The height of *R* is arranged so that its point can be easily brought into contact with the wick by slightly shifting the position of *B*. Now make the point of *R* red hot by holding it for a minute in the Bunsen flame, quickly insert the stopper, and move *B* so as to touch the match-head with the hot glass.[1] The candle burns for a time and then goes out. What alteration do you find in the volume of the air (*a*) while the candle is burning, (*b*) after it has gone out and the apparatus has become quite cold, (*c*) after it has been allowed to stand for some hours?

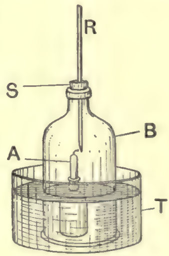


Fig. 23. — Experiment to find what proportion of the air is used up when a candle burns.

34. Is the Liquid which is formed the only Product?—Since we have seen that one product of the combustion of the candle is a liquid at ordinary temperatures we should expect to find some diminution in the volume of the air, for even the lightest of liquids occupies far less space than an equal weight of any gas. But the comparatively small amount of the diminution seems to point to one (or both) of two things—(*a*) it may be that the candle goes out before all the oxygen is used up; (*b*) it may be that besides the liquid another product is formed—a *gas*. The first possibility is very easily tested. We have only to pass a piece of phosphorus attached to a wire up into the gas in the bell-jar to show that it still contains much unchanged oxygen, for the phosphorus "smokes" and the volume of the gas diminishes. The second supposition may nevertheless also be correct, and it is supported by the fact that after the candle has ceased to burn and the apparatus become cold, the volume of gas

[1] If the candle be lighted first and the bell-jar then placed over it, as is sometimes recommended, the experiment gives quite misleading results, for the error caused by the expansion of the air in the bell-jar (chiefly *before* it is shut off by the water) is greater than the change of volume to be measured. An ordinary match-head gives no more than 3 or 4 c.c. of gas when ignited, so that the error from this source is negligible.

in the bell-jar continues to diminish slowly for some hours. This seems to point to the presence of a gas more soluble than oxygen. But since we began our experiment with air in the bell-jar, the bulk of the gas left over must be nitrogen; and we have no means of absorbing this nitrogen and leaving the new gas (assuming that there is one) in the pure state so that we may be able to examine its properties. What, then, is to be done? Clearly the best plan will be to repeat our experiment, using pure oxygen instead of air. Any gas left over must then consist of the products of combustion, mixed, perhaps, with a little unchanged oxygen.

Ex. 36.—Repeat the last experiment, but before lighting the candle pass a *brisk* current of oxygen into the bell-jar for several minutes so as to completely drive out the air. Light the candle as before, and note exactly what happens. Measure the contraction after the candle has ceased to burn, and the apparatus has become quite cold. Now pass small portions of the gas into test-tubes (see Fig. 24 for method of doing this) and find (*a*) its action on a lighted taper; (*b*) whether it is soluble in water; (*c*) what is its action upon litmus. For (*a*) use a rather wide tube, for (*b*) a narrow one which can be tightly closed by the thumb (see Ex. 33).

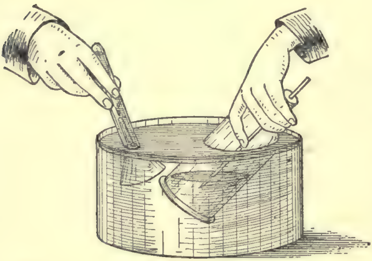


Fig. 24.—Transferring a sample of gas from a bell-jar to a narrow tube.

This experiment shows conclusively that the colourless liquid which we obtained when the candle was burned in a dry glass bottle is not the only product of the combustion. At least one other substance is formed—a colourless invisible gas, which extinguishes a burning taper, changes the colour of blue litmus to a wine-red tint, and is much more easily soluble in water than either air or oxygen. The last three experiments may be repeated with other combustible bodies, such as paraffin oil or methylated spirit, coal-gas, etc., and in every case we shall find the same result. The same two products are formed, though not in exactly the same proportions.

35. What is the Liquid which is formed by the Burning of a Candle?—Let us now turn our attention to the composition of the two new substances into which our candle has been converted. And first as to the liquid—it *looks* like water; but we shall make no progress in chemistry if we guess the composition of substances from their appearance. We have already seen that a black powder may contain silvery mercury and yellow sulphur, and that white, easily soluble crystals may contain metallic silver. How are we to make sure whether or not this liquid is water? Evidently we must test its properties, and for this purpose we must first obtain a larger quantity of it. In order to do so we must keep in view two things:—first, the candle must have a constant supply of air, so that it may go on burning for a considerable time; and, secondly, we must arrange some means of cooling the gases which are given off from the flame, since it is evident that any liquid which may be present will be in the form of vapour and must be condensed.

Fig. 25.

Ex. 37.—Repeat Ex. 34, but before the candle goes out put into the neck of the bottle a piece of thin sheet metal or cardboard cut to the shape shown in Fig. 25. The candle will now go on burning for an indefinite time. How do you account for this? Notice what happens to the deposit of liquid on the sides of the bottle. Why does it disappear after a while?

Fig. 26.—Collecting the water formed by the burning of a candle.

Now arrange the apparatus as shown in Fig. 26. The tall jar is sunk nearly to the brim in a large jar (a bucket will do) of cold water. This may be done by twisting a piece of lead piping round it, or in any other convenient way. The candle is lighted and lowered to the bottom of the jar by a wire, the piece of card is inserted at the mouth, and the candle is left to burn for at least half-an-hour. (An alternative apparatus for this experiment is shown in Fig. 27; but it is somewhat more troublesome to fit up, and requires a stream of water from the tap.)

When sufficient liquid has collected, proceed to examine it. What is its appearance? Take out a drop on a glass rod and put it on the tongue. Has it any taste? Determine its density by measuring out 2 or 5 c.c. with a pipette and weighing it. Distil it and determine what the boiling-point is, and whether it is constant, and the liquid therefore (see Chap. III.) a pure substance. Determine also its freezing (melting) point. How do your results agree with those given by pure water?[1]

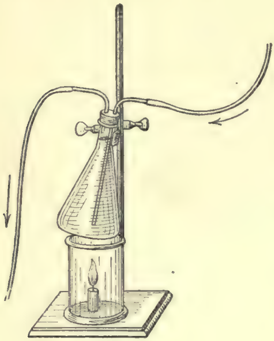


Fig. 27.

36. Is Water an Oxide?—It follows from these experiments that the liquid formed when a candle (or any ordinary combustible) is burned in air is water. And since the chemical change that occurs in the combustion is a union with oxygen, it follows that in all probability water is an *oxide*—a compound of oxygen with some element (or elements) which is present in all ordinary combustibles. How can we separate this other element from the oxygen and obtain it in the "free" or uncombined state? The most likely way would seem to be by acting upon the water with some element which has a great "affinity" for oxygen—*i.e.* combines very readily with it. Magnesium is such an element. We have already seen that it burns brilliantly in oxygen (or even in air), forming a white powder which is almost insoluble in water, but has the power of turning neutral litmus solution to a deep blue colour. If we light a piece of magnesium and plunge it into water it will be extinguished, as might be expected, for we have seen that the metal does not combine with oxygen at ordinary temperatures but only at a red heat, and to plunge the metal into water at once reduces its temperature to that of the water. But can we not

[1] *Note for the Teacher.*—As in all similar cases, these experiments should be divided among the class, some being told off to determine the density, others the freezing-point, and others the boiling-point. The results should then be shown on the blackboard and discussed by the whole class.

use the water in the form of *gas*? In this form the experiment seems more hopeful.

Ex. 38.—Boil a little water in a wide-necked flask of one to two litres capacity, and wait till steam issues freely from the mouth. Plunge a lighted taper fastened to a piece of soft iron wire into the steam. What happens? Now take a piece of magnesium wire or ribbon, light it at one end in the Bunsen flame and plunge it into the steam. Notice exactly what happens. Compare the white powder with that which you obtained in Ex. 31 by burning magnesium in oxygen. Try its action upon litmus solution.

37. How can we separate the other Element contained in Water?—If the white powder obtained in the last experiment is really magnesium oxide—and the more carefully it is examined the more certain does this become—the experiment proves conclusively that water contains oxygen. But what of the other element with which we have reason to think the oxygen must have been combined? Have you seen any evidence of its existence? Probably not; and therefore it seems most likely that it, like oxygen, is an invisible gas. We must therefore repeat the last experiment in such a way as to enable us to collect and examine any gas that may be formed.

Ex. 39.[1]—Fit up the apparatus shown in Fig. 28. *F* is the flask used in the last experiment. *S* is a rubber stopper which fits it easily, and through which passes a bent glass tube connected by a long rubber tube to the glass tube *T*, which passes under the water of the pneumatic trough. (All these tubes should be of rather wide bore, otherwise there is some danger that the pressure may blow out the stopper, or even burst the flask.) The spiral of magnesium wire (ribbon is not so suitable for this experiment) is held by pushing its end between the rubber of *S* and the bent tube *L*. When all is ready, boil the water in *F* as before, light the magnesium and plunge it quickly into the steam. As soon as the stopper closes the neck of the flask, bubbles of gas pass through the water and collect in *A*. Continue to heat *F* until nothing but steam is passing over (how can you tell when this point is reached?), and then lift out the leading tube *T* from under the water and *afterwards* remove the lamp. (If the lamp were removed

[1] To be done by the teacher only, or under his immediate supervision.

first the steam would condense and cold water would be forced by atmospheric pressure from the trough into *F*, which would probably break the flask.)

It seems probable that the colourless gas which we have

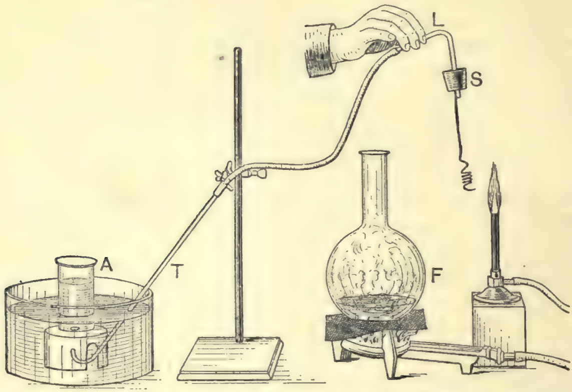


Fig. 28.—To collect the gas which is set free when magnesium burns in steam.

collected in the jar in the last experiment is the substance for which we are seeking. Pour some of it from the jar into a smaller jar or a wide test-tube (see Fig. 24 for method of doing this). Plunge a lighted taper quickly into the jar. What happens? Repeat the experiment with a fresh jar of the gas held *mouth downwards*. What difference do you notice, and what inference may be drawn as to the density of the gas compared with that of air? To prove that the gas is lighter than air, fill a third jar, and try to pour the gas upwards into another which is "empty"—*i.e.* full of air (see Fig. 29). Test each jar with a light. Where has the inflammable gas gone? Find out also whether the new gas is soluble in water.

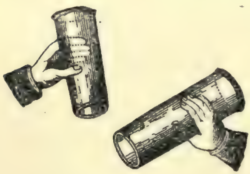


Fig. 29.

When we burned magnesium in an open flask filled with

steam we saw no evidence of the presence of the new inflammable gas. We can now understand the reason, for the gas itself is quite invisible and its flame gives so little light (though you will have noticed that it is very hot) that it is quite difficult to see. If you repeat Ex. 38, covering the flask with a piece of cardboard or a thick cloth so as to shut off the dazzling glare of the burning magnesium, you will see that the new gas burns at the mouth of the flask with a large pale greenish flame.

38. **Analysis and Synthesis.**—We may now assert almost with certainty, that water is a compound of oxygen with the invisible gas set free by magnesium, which in future we shall call "hydrogen."[1] We have proved this by the process of replacing the hydrogen by another element having greater affinity for oxygen—namely, magnesium. Reactions such as this, in which a compound is split up wholly or partly into its elements, are examples of chemical analysis. We have already had good examples of analysis in the decomposition of mercuric oxide and silver nitrate by heat (Chaps. I. and V.). It is not always necessary to actually obtain the elements in the free state in order to analyse a compound. In this case, for example, we do not obtain free oxygen gas from the water. But since we got magnesium oxide formed from magnesium and water, and since we are quite certain that this substance is a compound of magnesium and oxygen, the proof that water contains oxygen is just as satisfactory as if we had actually obtained oxygen gas from it. To confirm our proof we shall afterwards have recourse to the opposite process of **synthesis**, by which is meant the building up of a compound from its elements. Of this process we have also had examples—for instance, the formation of mercuric sulphide from its elements (Ex. 1), the formation of the oxides of sulphur, carbon, etc. (Ex. 31), and others.

To carry out the synthesis of water we must burn hydrogen in oxygen and show that water is formed. This we shall proceed to do; but first it will be convenient to study the properties of hydrogen a little more fully and to give some other methods of obtaining it.

[1] From the Greek *hudōr*, water, and *gennaō*, to produce.

39. Other Methods of preparing Hydrogen.—Magnesium is not the only metal which can take out the oxygen from water and set free the hydrogen. Iron can do the same. But you will not succeed in getting an iron wire to burn in steam. It is necessary to pass the steam through an iron or hard glass tube filled with iron filings or iron wire gauze which must be kept at a red heat by a gas flame (see Fig. 30). There are other metals, not so common as iron, which can act chemically upon water even at the ordinary temperature. Sodium is one of these. It is a soft metal, with a lustre like silver, and combines with oxygen so readily that it can only be kept under petroleum or some other liquid free from oxygen.

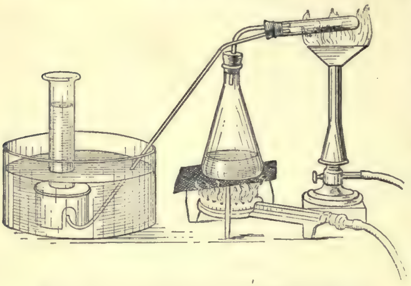


Fig. 30.—Preparation of hydrogen by heating iron filings in steam.

Ex. 40.—Cut off a piece of sodium *not larger than a small pea*[1] and throw it on the surface of a few c.c. of water contained in a small porcelain basin. Notice and describe exactly what happens. (It is well to shield the eyes by a glass plate, as particles are sometimes thrown out with considerable violence.) Was any gas given off? Repeat the experiment and try to light the gas. What do you notice as to the appearance of the small globule that remains at the end of the experiment after the hissing sound has ceased? What becomes of the sodium? Has the water acquired any new properties? (Try its effect on litmus and on the fingers.) The liquid should be evaporated (best in a clear nickel or silver basin) and the residue examined.

Ex. 41.—Repeat the last experiment, using a *very small* piece of potassium (a soft metal very like sodium in appearance and properties). Describe all that takes place, noting the points in which the two actions resemble and those in which they differ from each other.

Ex. 40. may be modified so that the hydrogen can be

[1] It is very dangerous to use a larger quantity of sodium.

collected and identified by its properties. The sodium may be held down under the water by wrapping it tightly in several folds of lead foil, or may be tightly packed into a piece of lead pipe one or two inches in length, which has been closed at one end by a blow from a hammer. In either case a jar full of water is held over the metal and the bubbles of gas are thus collected. By comparing the properties of the gas thus prepared with those of the hydrogen obtained from water by the action of magnesium it can easily be shown that the two gases are identical.

We have now a choice of four different ways of preparing hydrogen, all, however, alike in this, that the hydrogen is set free from water by the action of a metal. But none of these methods can be called very convenient, and we shall now go on to consider a different kind of action—that of metals upon a class of bodies called acids—by which in many cases we can get hydrogen more conveniently.

40. Common Acids.—The exact definition of what constitutes an acid had better be left till later. For the present we shall confine ourselves to the study of three of the commonest, all of which are corrosive liquids, having a sour taste when largely diluted with water, and having also the property of changing the colour of blue litmus solution to a bright red. Their names are sulphuric acid or oil of vitriol, nitric acid or aqua-fortis, and hydrochloric acid.

Sulphuric acid, as its name implies, is made from sulphur. The process of manufacture will be mentioned later on. The name oil of vitriol refers to the oily thick consistency of the liquid and to the fact that it can be prepared by strongly heating "green vitriol" in a retort and condensing the vapours that are given off.

Ex. 42.—Examine a sample of this acid. Notice its oily consistency. Find its relative density. Take out a drop on a glass rod, and put it on a piece of waste cloth—what happens? Pour some slowly into a beaker containing water—what do you observe? Put a few drops into a glass of water and taste the mixture—also test it with litmus solution or paper. Heat a few drops in a test-tube and notice and describe what happens. Pour 20 or 30 c.c. into a shallow glass dish, weigh the whole, leave it exposed to the air for some hours and then

weigh again. How do you account for the increase? Now place the dish along with a similar dish containing water, also carefully weighed, on a piece of plate glass and cover both with a bell-jar having a ground rim which has been previously well greased. Weigh both dishes again after a few hours. Explain what has happened.

These experiments will show you that sulphuric acid is a substance to be treated with great respect. Great care must be taken to avoid getting any of it on the skin, and should any do so, it should be *at once* washed off by a copious stream of water from the tap. Should any fall on the clothes the place should be sponged with strong ammonia solution. When sulphuric acid has to be diluted with water it must always be poured gradually in a thin stream *into the water*, not *vice versâ*; otherwise the sudden evolution of heat may cause an explosion, and some of the acid may be scattered about.

Nitric acid is prepared from nitre or saltpetre by heating it with sulphuric acid and condensing the vapour which is given off.

Ex. 43.—Put about 15 c.c. of strong sulphuric acid into a stoppered glass retort, using a glass funnel. Add by means of a paper gutter about 20 gm. of nitre, and put the beak of the retort into a test-tube kept cool by immersion in a flask of cold water. Now heat the bulb of the retort and notice what happens. When no more liquid collects in the test-tube, stop the experiment, pour the contents of the retort into a porcelain basin and examine the liquid in the test-tube as you did the sulphuric acid. What is its appearance, its relative density? How does it act upon cloth, on the skin, on litmus solution? What happens when it is mixed with water; when it is heated in a test-tube?

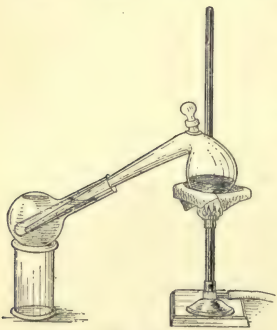


Fig. 31.

Hydrochloric acid.—The method of preparing this acid will be described later. Meanwhile a sample of the concentrated acid should be examined like the other two and the resemblances

and differences carefully noted. All three acids are dangerous unless carefully handled, and they must therefore be used with caution. Two of them (which?) give off corrosive fumes even at the ordinary temperature, and all are violent poisons when in concentrated form, though harmless when *very* largely diluted with water.

41. The Action of Acids on Metals.—Having now obtained some knowledge of the more obvious properties of the three common acids, let us next try an experiment which is performed by the plumber when he makes what he calls "killed spirits of salt," for use as a flux in soldering.

Ex. 44.—Put some strong hydrochloric acid into a test-tube (a depth of a quarter of an inch is quite sufficient), add an equal volume of water, and drop into it a small piece of zinc (foil or thin sheet should be used). What happens? Find out what you can as to the properties of the gas which is given off. When the zinc has disappeared put in another small piece, and repeat this till the last piece of metal remains unchanged.

The zinc is usually said to "dissolve" in the acid. Is this a case of ordinary solution such as we have discussed in Chapter II.? How can you find out? Evidently only by evaporating, and comparing the residue that is left with the substance with which you began. Do you get back the original substance? It is clear that this is not a case of ordinary solution, but of what is sometimes distinguished as "chemical solution," where a substance is chemically acted upon and converted into a new substance which then dissolves.

The last experiment should be repeated first with dilute sulphuric acid, then with strong sulphuric acid, and afterwards with nitric acid, using each first dilute and then strong. In each case all that happens should be carefully noted and described. Is hydrogen evolved? is any other gas? Similar experiments may also be made with other metals, such as magnesium, iron, copper, tin, and lead. The metals should be used in thin foil or wire, and the acids should be heated in case there is no action in the cold. The results of the experiments should be drawn up in tabular form so as to show what kind of action takes place between each metal and each acid, thus:—

Acid used	Description of Action with		
	Zinc	Magnesium	Copper
Hydrochloric (Strong)	Violent effervescence in the cold — Hydrogen evolved. A white soluble substance formed.		
Hydrochloric (Dilute)			

In every case where the metal "dissolves," the solution should be evaporated and the residue described. It may then be labelled and put aside for future study.

It will be found that when a metal is acted upon at all by hydrochloric acid or by *dilute* sulphuric acid, hydrogen is given off and a soluble "salt" containing the metal remains in solution; that *strong* sulphuric acid gives a quite different action, a heavy gas with the suffocating smell of burning sulphur being evolved; and that nitric acid "dissolves" most of the metals, but in almost no case gives hydrogen.[1]

42. Preparation of Hydrogen.—We shall return later to the subject of the action of metals upon acids. Meanwhile we are only concerned with it as furnishing the most convenient means of preparing hydrogen. For this purpose the materials generally used are zinc clippings and dilute sulphuric or hydrochloric acid.

Ex. 45.—Fit up the apparatus shown in Fig. 32. Put about 5 gm. of zinc clippings into the bottle, pour dilute hydrochloric or sulphuric acid through the "thistle funnel," and collect several jars of the gas over water in the usual way. Keep the first two, which will contain hydrogen mixed with

[1] An exception is the case of cold dilute nitric acid acting upon magnesium, which gives nearly pure hydrogen.

air, separate from the others. Test the first jar with a light. How do you account for the result? Try to find out what proportions of air and hydrogen give the sharpest explosion. Remembering that air contains only one-fifth of its volume of oxygen, calculate what proportions of hydrogen and *oxygen* would give the sharpest explosion.

Ex. 46.—Support one of the jars of hydrogen, *mouth downwards*, on a tripod or other convenient stand. Leave it for a quarter of an hour and then test with a lighted taper. You will find that all the hydrogen has escaped.

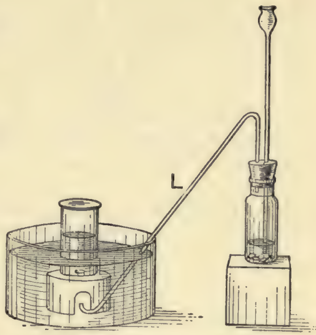


Fig. 32.

The last experiment illustrates a property which all gases possess —that of mixing spontaneously with each other. This property is known as *diffusion*. Hydrogen possesses it in a very special degree, and in consequence this gas is particularly difficult to prepare and preserve in a pure state, for diffusion takes place not only when the gas is exposed to direct contact with air, but also more slowly through all porous materials such as cork, wood, paper, and even india-rubber.

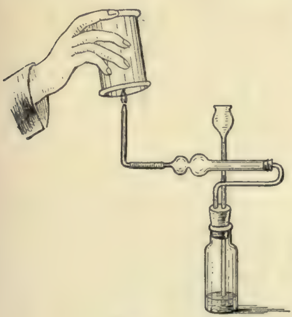


Fig. 33.

43. Synthesis of Water from Hydrogen and Air.

Ex. 47.—Remove the leading tube *L* from the hydrogen apparatus and replace it by the tube shown in Fig. 33, which is filled with small pieces of pumice-stone moistened with strong sulphuric acid, and has a jet of hard glass tubing attached to it. The hydrogen will pass through the sulphuric acid, and in doing so will be freed from the water vapour which always accompanies it, and which may form a consider-

able proportion of its weight if the liquid in the generating flask be allowed to get hot. Hang a test-tube over the jet for a minute and then remove it and test the gas in the tube with a light. If it burns quietly after only a slight "pop" when the light is put to it we may assume that the hydrogen in the flask is free from air. Now put a light to the jet[1] and hold over the flame a cold beaker or bell-jar. What do you notice? How could you collect a large quantity of the liquid which is produced, and how would you prove it to be water? (See pp. 51 and 52.)

44. Quantitative Synthesis of Water.—Our proof of the composition of water is now complete. We have shown that it can be split up into oxygen and hydrogen, and we have seen its formation by the union of the same two elements. But so far our proof is *qualitative* only—we have shown that water is composed of hydrogen and oxygen, and of nothing else; but as yet we have found out nothing as to the proportions in which the two elements combine, except what may be argued from the very rough experiment No. 45 (p. 61). We shall next make experiments to find out the proportions by volume in which the two gases combine. For this purpose measured volumes must be mixed and exploded in a vessel shut off from the air. The explosion is best brought about by an electric spark, which gives us a convenient method of heating a portion of the mixed gases up to the temperature at which chemical action takes place between them, without opening the tube in which they are contained, as we should be obliged to do if we used a lighted taper. The apparatus used is called a eudiometer, and the particular form which we shall employ is known as Hofmann's, from its inventor. It consists essentially of a glass tube bent in the form of a U, and

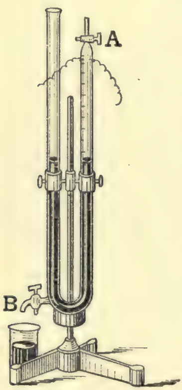


Fig. 34.

[1] *Great care must be exercised* in making quite sure that all air is expelled before lighting the hydrogen at the jet, otherwise an explosion will occur which will shatter the apparatus and may do serious injury to the experimenter. It is safer to use a thin glass flask for this experiment, since if an explosion *should* occur the thin glass is less likely to do mischief.

having two thin platinum wires passing air-tight through the glass so as nearly, but not quite, to meet inside the tube. The gases are shut off by mercury or water in the bend of the tube; and by connecting the platinum wires to the poles of an induction coil or a charged Leyden jar we can pass a spark through them at will.

Ex. 48 (*Teacher only*). — Fill the eudiometer (which should be perfectly clean and dry, and should have the taps well greased with a little vaseline) completely with clean dry mercury,[1] and close the tap *A*. Now open tap *B* and allow the mercury to run out until the open limb is nearly empty. Make sure that the level of the mercury remains steady, showing that no air enters at *A*. Now put some zinc foil and dilute hydrochloric acid into a test-tube furnished with a cork and long delivery tube, and pass the latter through the open limb of the eudiometer to the bend. Allow the hydrogen to escape for several minutes to make sure that all air is expelled from the tubes, and then tilt the eudiometer so that the bubbles of hydrogen pass up into the closed limb. When 20 or 30 c.c. have passed in remove the test-tube. We have now to find the volume of this hydrogen at the temperature and pressure of the laboratory. To do this we must pour mercury into the open limb until the level in both limbs is the same. When this is the case the volume of the hydrogen is carefully noted. Now run out the mercury again from *B* and pass in, in the same way, about 8 or 10 c.c. of pure oxygen, made by heating potassium chlorate (alone) in a test tube of hard glass. Adjust the level of the mercury once more (why is this necessary?) and read off the volume of the mixed gases. The difference between this and the volume of the hydrogen alone will, of course, be the volume of oxygen taken. Now close the mouth of the eudiometer *tightly* with an india-rubber stopper or a good cork to prevent the mercury from being

[1] All experiments with mercury should be done over a tray of wood or iron, so that any mercury that is spilt may be easily recovered. Great care must be taken to keep mercury from contact with other metals (except iron and platinum) with which it combines readily. The presence of other metals is shown by the dull surface of the mercury and by the tendency of the drops of metal to cling to the glass of the apparatus and form a "tail." Impure mercury may be purified by covering it with a layer of very dilute nitric acid and leaving it for several days, with occasional shaking.

forced out by the explosion, run out some mercury from B so as to reduce the pressure within the eudiometer, and, lastly, connect the platinum wires to the coil or Leyden jar and pass the spark[1] through the mixed gases. Note exactly what happens. Take out the cork, adjust the pressure as before, and read off the volume of gas left in the eudiometer. What else can now be seen inside the tube? Lastly, fill up the open limb completely with mercury, close it tightly with the thumb, and invert the apparatus so that the gas passes round the bend into the open limb. Test it with a lighted taper. What is it? State the results thus:—

(a) volume of hydrogen taken	c.c.
(b) ,, of mixed gases before explosion . .	c.c.
(b) – (a) = vol. of oxygen taken . . .	c.c.
(c) vol. of hydrogen left after the explosion . .	c.c.
∴ vol. of hydrogen which has combined with the oxygen ($= a - c$)	c.c.

The experiment should be repeated, reversing the proportion between the two gases—*i.e.* using 20 to 30 c.c. of oxygen, and 10 to 15 c.c. of hydrogen. Water may be used instead of mercury when the experiment is repeated by pupils, but the results in this case will be somewhat less accurate, especially when excess of oxygen is used, owing to some of the gas being dissolved at the high pressure produced by the explosion; moreover, the water formed by the union of the two gases cannot in this case be observed.

When the results of the experiments with the eudiometer are tabulated, it will be found that no matter what the proportions may be in which the two gases are *mixed*, they combine always in one fixed and definite proportion—two volumes of hydrogen to one of oxygen. If we take 20 c.c. of hydrogen to 10 c.c. of oxygen, the whole of the gases disappear and only liquid water is left. If we take 21 c.c. of hydrogen to 10 c.c. of oxygen, then 1 c.c. of hydrogen is left over. If we take 20 c.c. of hydrogen to 11 c.c. of oxygen, then 1 c.c. of oxygen is left over. But by no means whatever can we persuade any given volume of hydrogen to combine with more or less than exactly half its own volume of oxygen.

45. Mixture and Combination.—These experiments furnish a

[1] As a precaution against possible accidents it is well to cover the eudiometer with a cloth before passing the spark.

striking example of the difference between chemical combination and mere mechanical mixture. We can *mix* oxygen and hydrogen in any proportions we please, and the properties of the mixture will vary according to its composition, exactly as in the case of oxygen and nitrogen. But the moment that even a small part of the mixture is raised to the "ignition point"—the temperature at which chemical action begins—the case is entirely altered. Combination takes place only in the fixed proportion already stated, and the excess of whichever gas was present in greater proportion is left over unchanged. The properties of the compound formed by the union of the two gases are quite different from those of either of its constituents and are as fixed and unalterable as those of any element. In fact we may take water as a typical example of a chemical compound, just as air is a typical example of a mechanical mixture. (See pp. 17 and 20.)

46. Composition of Water by Weight.—It is evident that the results of these "volumetric"[1] experiments can be used to find out the composition of water *by weight* if only we know the relative densities of the two gases. The weight of a litre of hydrogen can be found by experiment exactly as in the case of nitrogen (p. 43). Care must be taken to dry the hydrogen thoroughly by passing it through a long tube containing pumice and sulphuric acid, and a large flask made of thin glass should be used. Even with the greatest care it is difficult to get very accurate results in the case of hydrogen, for the weight of a litre is extremely small, and there are numerous sources of error, such as impurities in the gas, condensation of moisture on the surface of the flask, and so on. The most accurate experiments have shown that the weight of a litre of hydrogen at N.T.P. (see p. 42) is ·0899, or almost exactly ·09 gm. That of a litre of oxygen under the same conditions is 1·44 gm., and it follows, therefore, that a given volume of hydrogen weighs almost exactly one-sixteenth as much as the same volume of oxygen under the same conditions of temperature and pressure.

47. Standard of Density for Gases.— No other known gas is so light as hydrogen, and it is therefore usually taken as the

[1] Dealing with measurements of volume.

standard of density for gases, just as water is the standard for liquids and solids. If we take the relative density of hydrogen as = 1, that of oxygen will be 16, and that of nitrogen 14.

We are now in a position to calculate the composition of water by weight. It is evident that if water were composed of *equal* volumes of oxygen and hydrogen, its composition by weight would be 16 parts by weight of oxygen to 1 part by weight of hydrogen. But the actual proportion by volume is one volume of oxygen to *two* volumes of hydrogen, and the proportion by weight is therefore 16 parts by weight of oxygen to 2 parts by weight of hydrogen, or 8 to 1. The same result may be got thus:—Since ·09 gm. of hydrogen measures one litre, one gramme will measure $\frac{1}{.09} = 11·1$ litres. We know from our experiments with the eudiometer that this volume of hydrogen will combine with 5·55 litres of oxygen; and the weight of 5·55 litres of oxygen will be $1·44 \times 5·55 = 7·992$, or almost exactly 8 gm.—that is, one gramme of hydrogen combines with 8 gm. of oxygen.

Notice here that we actually put out fires by throwing on to the burning mass a liquid containing $\frac{8}{9}$ of its weight of oxygen —more than three times the proportion contained in air! A more striking example of the change in properties produced by chemical combination would be hard to find.

Notice also that from 16·65 litres (nearly four gallons) of the mixed gases we get only 9 c.c. of liquid water.

48. Direct Proof of the Composition of Water by Weight.— The composition of water by weight may be proved in a more direct manner. The most direct would be to burn a weighed quantity of hydrogen and collect and weigh the water produced. But this is difficult to carry out in practice, owing to the lightness of hydrogen and the consequent difficulty of weighing it accurately. It is easier to find how much water can be got from a given weight of oxygen, though even in this case the oxygen is best weighed in the solid form, in combination with a metal.

Ex. 49.—Hold a piece of thin copper foil in the extreme edge of a Bunsen flame for a few seconds. Let it cool, and notice what has happened to the metal. Bend the foil backwards and forwards—what do you notice? Now take a porcelain crucible, just large enough to take in the bowl of an

ordinary clay tobacco pipe, put into it a few grammes of clean copper foil, and weigh the whole carefully. Heat the crucible on a triangle, resting it on its side so that air may enter freely, and after ten minutes or so allow to cool and weigh again. How do you account for the increase? Next connect the clay pipe by a few inches of rubber tubing to an apparatus giving a brisk current of hydrogen, and *when you have made perfectly sure that all air is expelled from the apparatus* place the inverted pipe bowl inside the crucible so that the partly oxidised copper may be heated in an atmosphere of hydrogen. After two or three minutes remove the lamp and allow the crucible to cool in the current of hydrogen.[1] Weigh the crucible and afterwards examine the contents. What has happened? What has probably become of the oxygen which was combined with the copper?

The last experiment furnishes the first step to a method for the "gravimetric" synthesis (*i.e.* synthesis *by weight*) of water, for if we heat copper oxide and pass hydrogen over it, the oxygen of the copper oxide will unite with the hydrogen to form water, leaving metallic copper. The water can be collected and weighed; the weight of oxygen in it is given by the loss of weight of the copper oxide, and the weight of the hydrogen will be the difference between this and the weight of the water.

The apparatus used is shown in Fig. 35. The hydrogen must be carefully dried by sulphuric acid. The copper oxide, which should be made from wire, not in powder, is contained in a narrow tube of hard glass (*C* in Fig. 35), and this is connected to a small, carefully weighed tube *K*, furnished with a bulb in which most of the water condenses, and a U-shaped portion filled with pumice moistened with sulphuric acid, which serves to retain the water vapour that escapes condensation in the bulb. Lastly, the tube *T* dips into a little strong sulphuric acid in a small jar, in order that no moisture from the air may pass backwards into the drying tube *K*. To get accurate results with this apparatus requires some care and patience. It has to be remembered that copper oxide is hygroscopic (*i.e.* has the property, like sulphuric acid and oxide of phosphorus, of absorbing moisture from the atmosphere), and care must be taken always to cork it up while hot. The stoppers must be removed only when the tube is about to be weighed. Care

[1] Coal-gas, which contains a large proportion of hydrogen, may be used instead of it for this experiment.

must also be taken to keep the end of the tube *C* sufficiently warm to prevent water from condensing in it, and yet not as hot as to burn the india-rubber tube which connects it to *K*.

The most careful experiments, carried out with many precautions that cannot be explained here, have confirmed exactly

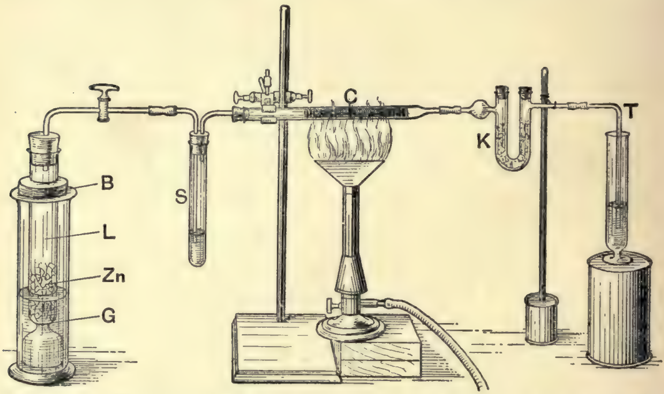


Fig. 35.—Experiment to find the quantitative composition of water by heating copper oxide in hydrogen. [The lamp chimney *L* contains pieces of zinc (*Zn*) supported by a piece of copper wire gauze at *G*. *B* is a cork (not air-tight) which supports *L* in an ordinary gas jar containing dilute acid.]

the results calculated from the volumetric experiments—that is, they show that eight parts by weight of oxygen combine with one part by weight of hydrogen. In other words, water is composed of 11·1 per cent. of hydrogen, and 88·9 per cent. of oxygen by weight.

49. Oxidation and Reduction.—The action of the hydrogen in the last experiment is a typical one. Many other oxides of metals, when heated in hydrogen, have their oxygen removed to form water, and are **reduced** to metal. The process of getting a metal from its oxide in this way is spoken of as **reduction**, and hydrogen and other bodies which act similarly in removing oxygen from compounds are called **reducing agents**. The opposite process, that of converting an element into its oxide is called **oxidation**, and substances such as potassium chlorate,

which readily give up their oxygen to other bodies, are called **oxidising agents.** It is evident, however, that the two processes usually go on together—for example, in the last experiment the copper oxide is said to be reduced by the hydrogen; but it would he equally correct to say that the hydrogen is oxidised by the copper oxide. Other examples of reduction and oxidation will be met with later on.

50. Electrolysis of Water.—We have now proved the quantitative composition of water in two different ways. There is still another experiment which is generally quoted as a "proof" of the composition of water. This is the process of decomposing "water" by the electric current. The apparatus for this experiment is shown in Fig. 36. The three-limbed glass tube is filled to the level of the taps *a* and *b* with dilute sulphuric acid, and the platinum plates are connected, by wires passing through the glass, to the poles of a battery of four or five Bunsen cells, connected in series. When the current passes from one platinum plate to the other, *which it can only do by passing through the liquid*, bubbles of gas appear at each plate and collect in the tube above it, while the liquid which is displaced is forced up into the bulb *C*. The gas which is evolved at the kathode (*i.e.* the plate connected to the *zinc* of the battery) is found to have approximately twice the volume of that which collects over the anode. By opening the taps the gases can be collected and tested, when it is found that the gas evolved at the kathode is hydrogen, and the other oxygen. If the experiment be tried with pure water, the current refuses to pass through it, and nothing happens. This experiment is a very interesting one, and may be regarded as a confirmation of the results obtained by those already described, but it can hardly be considered to *prove* anything;

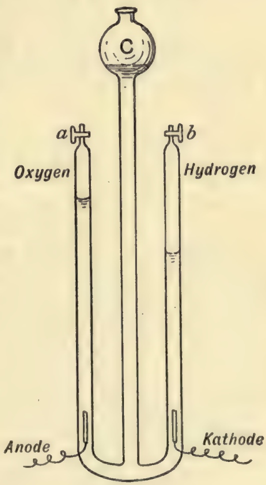


Fig. 36.

for what is used in the experiment is not pure water at all, but water plus sulphuric acid. Now sulphuric acid contains both hydrogen and oxygen, and there are no means—or at least no ready means—of proving that the hydrogen and oxygen we obtain in the electrolysis come from the decomposition of the water, and not from that of the sulphuric acid which has been added to it.

QUESTIONS AND EXAMPLES ON CHAPTER VII.

1. When a kettle full of cold water is placed over a gas flame, drops of liquid collect on the bottom. What is the liquid? What experiments could you make with it in order to identify it?

2. How do you account for the fact that a lighted taper is extinguished when plunged into steam, although steam contains $\frac{8}{9}$ of its weight of oxygen—more than four times the proportion contained in air?

3. What is meant by the term "analysis" in chemistry? Give two examples.

4. How would you prove by experiment that the air left after burning a candle under a bell-jar contains (*a*) unchanged oxygen; (*b*) another gas (besides nitrogen)?

5. What is meant by the term synthesis in chemistry? How would you carry out the synthesis of oxide of mercury?

6. Describe shortly three different methods of obtaining hydrogen from water. What experiments would you make in order to show its most important properties?

7. How would you distinguish a bottle of strong sulphuric acid from one of water, without opening either?

8. Give a list of the properties which are common to hydrochloric, nitric, and sulphuric acids.

9. Describe the action of (*a*) strong hydrochloric acid; (*b*) strong sulphuric acid, upon zinc.

10. If 25 c.c. of hydrogen be mixed with 9 c.c. of oxygen, and exploded in an eudiometer, what volume of gas will remain after the explosion, and of what will it consist?

11. If half-a-litre of hydrogen (measured at N.T.P.) be burned in the air, what weight of water will be formed?

12. What weight of hydrogen could be got from 18 gm. of water? What would be the volume of this hydrogen at N.T.P.?

13. What weight of oxygen is contained in 10 c.c. of water? What would be its volume at N.T.P.?

14. A tube containing copper wire gauze gains ·24 gm. in weight when heated in a current of oxygen. What weight of water will be formed by passing hydrogen through the heated tube?

15. Describe with a sketch how to show the "electrolysis of water." What are the objections to this experiment as a proof of the composition of water?

16. How would you show by experiment that sulphuric acid absorbs water vapour from the atmosphere when exposed to it?

17. What other substance has this property of absorbing water vapour?

18. Sketch the apparatus you would use for the gravimetric synthesis of water.

19. Can you suggest any experiment for finding the gravimetric composition of water by analysis?

20. Calculate (*a*) the weight at N.T.P., (*b*) the density, of a mixture of equal volumes of oxygen and hydrogen.

21. Distinguish between ordinary solution and "chemical solution," and give an example of each.

22. What would be the effect of passing a slow current of air through a tube containing red-hot copper? Sketch an apparatus that might be used for the experiment.

CHAPTER VIII

STUDY OF CHALK

51. Solid Substances that occur naturally.—Having now learned something of the composition and properties of the commonest gas (air), and the commonest liquid in the world around us, let us next turn our attention for a time to the solid substances found in nature. Many of these, as we have already seen (Chap. I.), are obviously mixtures, and the number of homogeneous solids found plentifully is comparatively small. Of these chalk may well be taken as a good example, because it occurs in large quantity, and is well known to most of us, because it was the subject of one of the earliest of the "classical" researches in chemistry, and because it is the raw material from which a very important substance—lime—is usually made.

Ex 50.—Begin by carefully examining a piece of chalk. Find out its relative density,[1] its hardness, whether it dissolves in water or acts upon litmus, whether it is crystalline or amorphous.

Ex. 51.—Find out what happens when chalk is treated (in a test-tube) with dilute hydrochloric acid. Warm the liquid and add more chalk in small pieces until no further effervescence occurs, and then test the solution with litmus. What change do you find? Evaporate the clear solution in a porcelain basin to dryness and examine the residue that is left. Is it chalk? Does it dissolve in pure water? What happens when a little of it is powdered and exposed to the air for an hour or two?

52. Action of Heat upon Chalk.—We have now learned

[1] Chalk is very porous, and unless some means be adopted of getting rid of the air it contains the relative density will be found much too low. The air may be expelled by putting the piece of chalk whose volume is to be determined into water, and either leaving it to stand for several days or placing it under the receiver of an air-pump and exhausting the air.

enough about the properties of chalk to recognise it with something like certainty. It is a soft solid with relative density about 2·7, practically insoluble in water, without action on litmus, and effervescing (*i.e.* giving off bubbles of gas) very strongly when treated with an acid. The solution so formed is neutral to litmus—*i.e.* it does not turn blue litmus red, as acids do, nor red litmus blue, as do magnesium oxide and the soluble substances which we obtained by the action of sodium and potassium upon water. We will next try to find out something about the action of heat upon chalk.

Ex. 52.—Heat a small piece of chalk strongly in a test-tube. Allow to cool, and examine it. Can you find any change in its properties? Probably not. Now take a piece of thin iron wire (about 0·5 mm. in diameter) and wrap one end of it three or four times round the point of a pencil, so as to make a conical spiral, large enough to hold a large pea. Put into the spiral a piece of chalk weighing not more than 0·1 gm., and support it so that the chalk will be heated as strongly as possible in a good Bunsen[1] flame. Hold it for three minutes in the hottest part of the flame and then take it out and allow it to cool. You will find little alteration in the *appearance* of the substance. But now put it on a watch-glass and add a few drops of water. What happens? Is heat evolved? Does the substance now act upon litmus? Is it soluble in distilled water? Does it effervesce with hydrochloric acid?

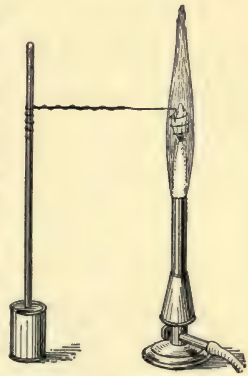


Fig. 37.—Conversion of chalk into quicklime.

53. Nature of the Change that occurs on heating Chalk.—It is clear that by heating the chalk we have converted it into a new substance differing entirely in its chemical pro-

[1] The burner must be in good order, and the flame should be a blue "roaring" one, containing nearly the maximum of air. The "Teclu" burner is very suitable, but any good Bunsen burner will do.

perties from the original chalk. The new substance is called quicklime (*i.e.* "live" lime, referring to its behaviour with water), and in this experiment we have done on a small scale what is done on a large scale in limekilns, where chalk or limestone is "burnt" to convert it into quicklime. We have next to ask ourselves what is the nature of the change that occurs. Does the chalk combine with oxygen or does it give up something to the flame? The answer to this question must be given by the balance.

Ex. 53.—Take a small piece of chalk (a long thin splinter is best) not more than 0·3 gm. in weight. Place it on a weighed watch-glass and find its weight as exactly as you can.[1] Now place it in the little iron wire spoon used in the last experiment, and heat it in the hottest part of the Bunsen flame for ten minutes.[2] Allow to cool, shake out the quicklime into a watch-glass, and weigh it at once. Calculate how much quicklime you could get from 100 gm. of chalk.

The following gives the particulars of an actual experiment carried out in this way:—

Weight of watch-glass alone	6·642 gm.
,, ,, + chalk	6·790 ,,
Weight of chalk taken	·148 ,,
Weight of watch-glass + quicklime	6·725 ,,
,, ,, alone	6·642 ,,
Weight of quicklime	·083 ,,

Then 100 gm. of chalk would give $\frac{\cdot 083 \times 100}{\cdot 148} = 56\cdot 1$ gm. quicklime.[3]

[1] Note that special accuracy is needed where the quantity used is so small. Your balance is probably liable to an error of at least 1 mgm. This would only be $\frac{1}{1000}$ of the whole if you were using 1 gm. of chalk, but it is $\frac{1}{100}$ or 1% of the whole when you use only ·1 gm.

[2] A convenient stand for holding the wire (see Fig. 38) can be made by placing a stout glass rod upright in one of the round tins used for vaseline, etc., and pouring round it plaster of Paris made into a cream with water. The free end of the wire is wrapped round a slightly smaller rod, into a cylindrical spiral, which can then be slipped on to the upright rod and will remain wherever it is placed. It is important that the part of the wire which is heated should not be more than ·5 mm. thick; but thicker wire may be used for the support, and is preferable, because less springy.

[3] *Note for the Teacher.*—If it is desired to use larger quantities of chalk a

This result shows that the change which chalk undergoes when heated in the air is not like that undergone by metals. The chalk does not combine with oxygen. On the contrary, it gives up 44% of its weight.

54. Action of Heat on Limestone, Marble, and Calcite.—It has been mentioned that quicklime is made from limestone as well as from chalk. The last two experiments may be repeated,[1] using limestone, marble, calcspar, arragonite, and pieces of oyster or other shells. It will be found that all these substances are essentially the same. Though they differ considerably in their physical properties, they all have the *chemical* properties of chalk, and all are converted by heat into quicklime, with the loss of 44% of their weight.

55. Is a Gas given off when Chalk is heated?—Since nothing can be *seen* to escape during the conversion of chalk into quicklime, it seems probable that a gas or vapour is given off. Unfortunately we cannot make sure of this by heating the chalk in a tube and collecting the gas, for we have seen that when heated in a tube the chalk remains practically unchanged. But perhaps the gas is identical with that given off when chalk is treated with acids? This seems all the more probable since we have seen that, after being heated, the chalk (or, rather, the quicklime into which it is converted) gives no gas when treated with acid. In order to test the point, we will next make an experiment to find out what weight of gas can be got from 100 gm. of chalk by the action of an acid.

Ex. 54.—Procure a small, light, wide-necked flask of about 100 c.c. capacity, and a short, wide test-tube which will stand inside it in a slanting position. The test-tube should hold about 10 c.c., and may be made by drawing out an ordinary $\frac{5}{8}$ in. test-tube in the blow-pipe flame (see Appendix, p. 180). Powder some dry chalk and put it into a dry test-tube furnished with a cork. Weigh this tube with its contents and note the weight. Now shake out about 1 gm. of the chalk into the flask. Weigh

muffle furnace must be used. The chalk may then be heated in small porcelain crucibles. It may be well to point out that the "chalk" used for writing on blackboards is usually not chalk at all, but a totally different substance.

[1] By different members of the class.

the tube again and subtract this from the original weight so as to find the exact weight of chalk that has been taken. Next put into the small test-tube about 6 or 8 c.c. of dilute hydrochloric acid (equal volumes of strong acid and water), make sure that the outside of the tube is dry, and let it down carefully into the flask, taking care to allow none of the acid to get out of the tube. (A thread may be tied round the tube and used to lower it into the flask.) Now close the mouth of the flask loosely with a large plug of cotton wool, allow it to get quite cold (you have probably warmed it by handling and so expelled some of the air it contained), and weigh it carefully. Having noted the weight, tilt the flask so that a little of the acid may flow out on to the chalk. Repeat this at short intervals till all the chalk has disappeared. The flask would now be ready to weigh were it not that it is now full of the gas, which may be heavier or lighter than air, and if so would cause a slight error in the result. Remove the cotton wool plug, put a short piece of glass tube into the flask (taking care not to touch the sides or the liquid) and suck out the gas. (Notice its taste. Have you ever tasted anything like it before?) Replace the plug, allow to cool, and weigh. Calculate what weight of gas would be given off by 100 gm. of chalk.

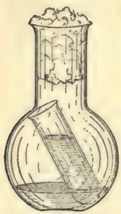


Fig. 38.

There are two principal sources of error in this experiment. The gas given off contains a little water vapour, and this will tend to make the result too high On the other hand, a little of the gas will remain dissolved in the liquid, and this will tend to make the result too low. Both errors will be small if the directions are carefully carried out, but the first one may become serious if the liquid is allowed to become warm.

56. Chalk a Compound of Quicklime and a Gas.—If the experiment is carefully done it will be found that the chalk gives almost exactly 44% of its weight of gas — the same proportion that is expelled by heat. We are therefore justified in assuming, for the present at least, that the gas given off when chalk is heated is the same gas that is set free from it by acids, and that, consequently, chalk is a compound of quicklime with this gas, in the proportion of 56 parts by weight of quicklime to 44 parts by weight of the gas. But what is the

gas? The next step is obviously to collect some of it and find out its properties and, if possible, its composition.

Ex. 55.—Using the apparatus employed for the preparation of hydrogen from hydrochloric acid and zinc (Fig. 32), collect over water several jars of the gas from chalk and hydrochloric acid. Find out its action upon a lighted taper, on litmus solution, its solubility in water, and whether it is heavier or lighter than air. (Pour it downwards from one wide-mouthed jar to another, and test with a light.) Have you previously examined any gas that has similar properties?

57. Can Chalk be formed by the Combination of the Gas with Quicklime?—If we are correct in assuming that this gas is the same that is given off when chalk is heated, it should be possible to get chalk once more by the combination of quicklime and the gas.

Ex. 56.—Take some freshly-heated quicklime, which must be free from chalk (test some of it with acid to make sure of this), place it in a mortar, and add a little water. Wait till the action is over, and then rub the "slaked lime" which remains with some more water, till it forms a smooth cream, known as "milk of lime." Take a few drops of this in a clean [1] test-tube, and pass into it for two or three minutes a stream of the gas made from chalk and hydrochloric acid. On now adding hydrochloric acid to the contents of the tube, you will find that it causes a brisk effervescence.

Ex. 57.—Put a few drops of the milk of lime into a watch-glass, and leave it exposed to the air for a few hours. Then test with hydrochloric acid. What happens? What do you infer as to the composition of the air?

Ex. 58.—Put a few c.c. of the milk of lime into a large volume of distilled water. Shake up, cork tightly, and leave it to stand for a day or two, with occasional shaking. Pour off the clear liquid, which is known as lime water, and pre-

[1] In all chemical experiments the greatest care must be taken to have all utensils perfectly clean. Test-tubes should be filled up with clean water and emptied again four times, and this must be done *after* using the brush to remove any solid that may be sticking to the sides. To show the necessity of this, put some strong sulphuric acid into a test-tube, pour it out, fill up with water, and repeat this until the water does not show any action on litmus. How many washings are needed? Yet litmus is not a very delicate test.

serve it in a tightly-corked bottle. Put a little clear lime water into a test-tube, and pass into it a few bubbles of the gas from chalk and hydrochloric acid. What happens? Pass in more gas, then boil the liquid, and filter off the "precipitate" of white powder. Test it with hydrochloric acid, and also by heating a few grains on iron wire, and placing it on moistened red litmus paper. You will find that the precipitate behaves in every way exactly like chalk.

These experiments show that when slaked lime, whether solid or in solution, is treated with the gas made from chalk and hydrochloric acid, a white powder is formed, which has the properties of chalk. To make absolutely certain that it is chalk, we may prepare a larger quantity of it by passing the gas into milk of lime until all the lime has been converted into the neutral powder (we can find when this is the case by testing with litmus, which will be turned purplish red as soon as all the lime has been acted upon), and then filtering off, washing and drying the powder, and testing it as in Ex. 54, to find whether it contains 44% of its weight of gas.

58. The Gas got from Chalk is also formed by burning a Candle or a Piece of Charcoal in Oxygen.—We have now proved beyond doubt that chalk is a compound of the soluble heavy gas with quicklime. We have next to find out what we can as to these substances themselves. Are they elements? In one case, at least, we can answer "no" with something like certainty, for the gas corresponds exactly in its properties to that which we obtained by burning a candle in oxygen, and also by burning charcoal in oxygen. We can easily show that the two gases are the same by burning a candle in a clean glass bottle, as in Ex. 34, and then shaking up the contents of the bottle with lime water. A milky precipitate of chalk is at once produced. The same result is given by the gas formed when charcoal is burned in oxygen.

59. The Gas contained in Chalk is an Oxide.—The last experiments point clearly to the supposition that the gas from chalk must be an oxide of carbon (charcoal is one form of the element carbon). Let us next try whether we can find any evidence of the presence of oxygen in the gas.

Ex. 59.—Fill a large jar with the gas, using the apparatus

shown in Fig. 39. [This method of collecting a heavy gas is called collecting "by downward displacement," and is used when a heavy gas is soluble in water or when it is required dry and we do not wish to use mercury as the fluid in the "pneumatic trough." Notice that the delivery tube must pass to the bottom of the jar so that the gas may not fall through the air and so mix with it, but may collect at the bottom and push the air gradually upwards and out at the mouth of the jar. Notice also, that owing to diffusion (see p. 61), a very brisk current of gas is required when using this method of collection. A good deal of the gas is therefore lost, and at the best the gas in the jar will always be mixed with a little air. The mouth of the jar should be covered with a card to prevent diffusion as much as possible.] When the jar is full, which may be roughly tested with a lighted taper, light a piece of magnesium ribbon and plunge it into the gas. What happens? Examine carefully the residue that is left in the jar. Is it pure magnesium oxide?

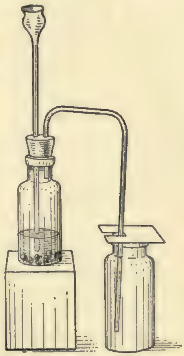


Fig. 39.

This experiment proves clearly that the gas from chalk is an oxide. It will also tell us what is the other element contained in the gas, for the black particles which are mixed with the white magnesium oxide can be collected and tested. They are easily separated from the magnesium oxide by adding dilute hydrochloric acid, which dissolves the latter but leaves the black particles unchanged. These are filtered off, washed and dried, and are found to consist of carbon. They burn in oxygen just as charcoal does, and the product of the combustion is the same gas which we have obtained by the action of acid upon chalk. In future, we shall call this gas by its chemical name of carbon dioxide.

The experiment of burning the carbon in oxygen may be made with the apparatus shown in Fig. 65. The black powder is placed in the hard glass tube, the gasholder is filled with oxygen, and the delivery tube dips into some clear lime water in a test-tube. On heating the tube the carbon glows brightly, carbon dioxide is formed, and a precipitate of chalk forms in the lime water.

By weighing the black powder beforehand, and passing the gas through a weighed tube containing moist slaked lime, it is possible to find what weight of carbon dioxide is formed from a given weight of carbon. This is almost exactly the method by which the composition of carbon dioxide has been actually determined. The results show that 12 parts by weight of carbon combine with 32 parts by weight of oxygen, forming 44 parts by weight of carbon dioxide.

60. Recapitulation.—We have now learned that chalk is a chemical compound of quicklime with carbon dioxide; that carbon dioxide is formed when chalk is heated or acted upon by an acid; that this gas is a compound of carbon and oxygen in the proportion of 3 parts by weight of carbon to 8 of oxygen, and that it is formed by the burning of a candle, of charcoal, and, indeed, of all ordinary combustibles in air or oxygen. Incidentally, we have also learned that this gas is present in small quantity in the air (Ex. 57), as, indeed, could be predicted from the fact that it is formed in all ordinary cases of combustion.

61. Volume of Carbon Dioxide contained in 100 gm. of Chalk.—Before leaving the subject of carbon dioxide, it will be interesting to make another experiment to find out what *volume* of the gas can be got from a given weight of chalk.

Ex. 60.—Fit up the apparatus shown in Fig. 41. *A* is a bottle of at least 500 c.c. capacity.[1] *B*, which may be of the same size or larger, is filled with water at the temperature of the room, and the tubes are so arranged that when the chalk and acid are brought together in *A*, the gas will expel its own volume of water from *B* into the jar *C*. All the stoppers must fit air-tight, and they had better be of india-rubber. In order to make sure that there is no leakage, blow a few bubbles of air through *E* into *B*, close the clip *D*, and leave the apparatus for five minutes. On opening *D* the water should rise in the tube *F*, and should remain at a constant level.

Weigh carefully a piece of tissue paper about three inches square. Put on it about 0·8 to 1 gm. of *powdered* chalk and weigh again. Put into *A* 8 c.c. of dilute hydrochloric acid (strong acid mixed

[1] The reason for using so large a bottle is that the carbon dioxide, being heavier than air, will remain near the bottom of the bottle and, provided its total volume is much less than that of the bottle, will not pass into *B* at all, but will remain in *A* and expel its own volume of *air* into *B*. Thus the error which would otherwise be caused by the solubility of the gas in water is avoided.

with an equal bulk of water). Open D, and suck water into the tube E (which should be drawn out to a jet at the bottom), till it is quite full; then close D again and put the empty jar C under the tube E. Wrap up the weighed chalk in the tissue paper so as to make a small bag, drop it into A, and *at once* put in the stopper tightly. Open the clip so that the water expelled by the gas may pass into C and be collected. Shake A so as to make sure that all the chalk comes into contact with the acid, and when there is no further action wait for ten minutes to make sure that the gas has cooled to the temperature of the room. Now raise the jar C till the level of the water in it is the same as in B. What happens, and why? Wait till the level of the water remains constant; then close the clip, and carefully measure the water. Note also the height of the barometer and the temperature of the room.

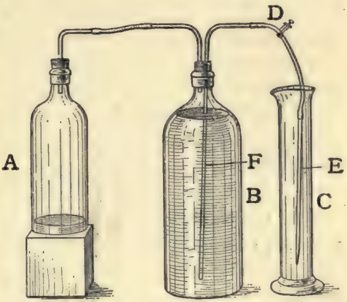


Fig. 40.—An experiment to find the volume of carbon dioxide contained in 100 gm. of chalk.

It will be found that at ordinary temperatures about 23·5 litres of carbon dioxide are given off from 100 gm. of chalk. Accurate experiments show that at N.T.P. the exact volume is 22·32 litres. Since we know from Ex. 54 that the carbon dioxide contained in 100 gm. of chalk, weighs 44 gm., it follows that 22·32 litres of carbon dioxide at N.T.P. weigh 44 gm., or 1 litre weighs $\frac{44}{22\cdot32}$ = approximately 1·98 gm. And since 1 litre of hydrogen at N.T.P. weighs 0·09 gm., carbon dioxide is $\frac{1\cdot98}{0\cdot09}$ or exactly 22 times heavier than hydrogen, bulk for bulk. This result can of course be confirmed by actually weighing a litre of carbon dioxide, as in Ex. 32.

62. Action of Water on Quicklime.—Let us now turn our attention for a time to the second substance which we have obtained from chalk—the quicklime. We have seen that, although not unlike chalk in appearance, quicklime differs very markedly from it in its behaviour with water. When a little water is poured upon this substance a great deal of heat is evolved, the quicklime swells up, cracks, and finally

[1] The volume at N.T.P. should be calculated, or found by using the volumeter described at p. 91.

forms a dry powder known as "slaked lime." How does this slaked lime differ from quicklime?

Ex. 61.—Heat a little dry slaked lime strongly in a dry test-tube. (See p. 4, as to the method of putting the powder into the tube without soiling the sides.) What do you see on the cold part of the tube?

Since water is given off when slaked lime is heated, it seems probable that the chemical action which takes place in the "slaking" of lime is a direct combination between the quicklime and the water. Let us try another experiment to find out whether this is so; and if so, what are the proportions in which the two substances combine.

Ex. 62.—Prepare a little pure quicklime by heating about 0·3 gm. of chalk in the Bunsen flame, as in Ex. 53. Meanwhile weigh a crucible. When the chalk has been heated for ten minutes put it into the crucible and weigh again. The difference between the two weighings will, of course, give the weight of quicklime used in the experiment. Now add a few drops of distilled water—sufficient to slake the lime and leave the residue moist—wait till the action is over and then put the crucible into an air-bath[1] heated to about 120° C. (see Fig. 41). As soon as the powder seems dry take out the crucible and cover it with a cold, dry, watch-glass. If the watch-glass is dimmed the contents of the crucible are not yet dry and it must be replaced in the air-bath. As soon as the watch-glass shows that the slaked lime is dry the crucible should be taken out, allowed to cool, and weighed as quickly as possible. After weighing add a drop of water to the powder. Does it behave like quicklime? Add now a drop of hydrochloric acid. Does it contain any chalk?

This experiment shows that when quicklime is slaked it gains in weight about 32%. (You will probably find a somewhat greater gain because the slaked lime will have combined with a little carbon dioxide from the air. To

[1] A satisfactory air-bath for such work may be made from an ordinary (unsoldered) tin canister such as is sold for holding tea. This is placed on its side upon a piece of wire gauze or asbestos cardboard, which can be supported on a tripod stand and heated by a Bunsen burner. A hole is cut in the top, through which a perforated cork, carrying a thermometer, is passed. The articles to be dried should be supported on a metal shelf an inch or so above the bottom of the canister.

get accurate results the drying should be carried out in a vacuum.) This water is not driven off when the slaked lime is heated to 120° C., though this is 20° above the boiling point of water. Hence this water must be chemically combined with the lime. But when we heat the compound to redness it is broken up and we get quicklime and water once more. We see from this that not only elements but also compounds may combine directly with other substances.

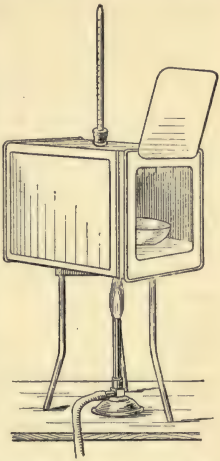


Fig. 41. — Air-bath made from a tea canister.

63. Laws of Chemical Combination.—These experiments furnish a striking example of the truth of the two fundamental laws of chemical combination—the law of the indestructibility of matter and that of combination in definite proportions. If we start with 100 gm. of chalk, we can split it up by heat into 44 gm. of carbon dioxide, and 56 gm. of quicklime. If we add to the 56 gm. of quicklime 18 gm. of water, we shall get 74 gm. of slaked lime; and if we act on this with 44 gm. of carbon dioxide, we can get once more the original 100 gm. of chalk and 18 gm. of water.

64. Lime Water.—We have seen that slaked lime dissolves in water, though only very sparingly. You will find that to dissolve 0·1 gm. of slaked lime you must use nearly 80 c.c. of cold distilled water (the water should have been recently boiled to expel all dissolved carbon dioxide). Lime water, as the solution is called, forms a very convenient test for the presence of carbon dioxide. By its means we can show that the gas is really given off (though only very slowly) when chalk is heated in a tube.

Ex. 63.—Heat some chalk very strongly in a hard glass test-tube, keeping the mouth of the tube loosely closed by the thumb. Dip a glass rod into some lime water, and insert it, with a drop of the clear liquid hanging to the end, into

the tube, taking care not to let it touch the sides. You will find that the drop of lime water becomes cloudy.

We can also show the formation of carbon dioxide in the burning of a candle very conveniently by means of lime water.

Ex. 64.—Repeat the experiment of burning a candle in a glass bottle. When the flame has gone out pour in some clear lime water and shake up. A milky "precipitate" of chalk will be formed. How could you make sure that it is really chalk? Repeat the experiment, using charcoal, a coal gas flame, methylated spirit, wood, or paraffin oil.[1] Do all these give carbon dioxide when burned in air?

65. Action of Acids upon Lime.—We have seen that quicklime dissolves in hydrochloric acid without effervescence. (Bubbles of *steam* may be produced, but these are easily distinguished, for they will not reach the top of the liquid if a relatively large volume of acid be used.) It will be interesting to find out whether the substance produced is the same that is formed when chalk is dissolved in hydrochloric acid.

Ex. 65.—Take 2 or 3 gm. of quicklime, slake it with a little water, and then add hydrochloric acid, a few drops at a time, and stir until a clear solution has been obtained. Evaporate the solution to dryness, and compare the properties of the solid thus obtained with those of the white "deliquescent"[2] substance formed by the action of chalk upon hydrochloric acid. You will find that the two bodies are identical.

The white substance formed in the last experiment, like oil of vitriol and phosphorus oxide (see pp. 57 and 28), has the property of absorbing moisture from the air, and is therefore often used for drying gases. (How could you prove that water is really absorbed when the calcium chloride deliquesces? Is there an increase in weight? Can the water be expelled again by heat?) Its chemical name is "calcium chloride"—calcium from the Latin *calx*, lime.

[1] A drop or two of the liquid should be poured on to a little asbestos supported in a deflagrating spoon.

[2] *i.e.* Having the property of deliquescing or becoming liquid when exposed to the air.

66. Is Quicklime an Element?—So far as our experiments have gone there is nothing to tell us with certainty whether quicklime is an element or a compound. It must be one or the other, for it has all the characteristics of a pure substance (see Chapter III.). It is not altered by even very intense heat, and this seems to support the idea that it may be an element. On the other hand, it does not resemble any of the common metallic elements such as iron, copper, zinc, magnesium, or lead, either in its physical properties or in its behaviour with acids, for we have seen that these metals, when acted upon by acids, always give either hydrogen or another gas. Lime, on the contrary, dissolves in hydrochloric acid without giving off any gas and forms a white, soluble, salt-like substance not unlike, in appearance and properties, the substances formed by the action of the same acid on zinc and magnesium. If we try to think of substances that *do* resemble lime, we shall probably be able to remember only one—magnesium oxide. This substance resembles quicklime in being a white, earthy solid unaltered by heat, and soluble in acids without effervescence, and also in having the property of changing the colour of moist red litmus-paper to blue. There the resemblance seems to cease. But perhaps it goes further—let us try whether magnesium oxide (or "magnesia," as it is usually called) resembles lime in its power of combining with water and carbon dioxide.

Ex. 66.—Take 2 or 3 gm. of magnesia (which may be bought, or may be prepared by burning a yard or two of magnesium ribbon over a sheet of glazed paper). Put it into a thimble or a very small crucible, moisten it with five or six drops of water, and stir the mixture with a thermometer. Is there any rise of temperature? How does it compare with that produced by the combination of water and quicklime? Leave the moistened powder exposed to the air till next lesson and then warm it with a drop or two of hydrochloric acid. What happens?

From this experiment it would seem that magnesia resembles quicklime in combining with water as well as in its other properties, and that the compound or "hydrate"[1] so formed, like slaked lime, combines with carbon dioxide from the

[1] A compound with water, from the Greek *hudōr*, water.

air, forming another compound which effervesces with acids.[1] These facts point to a very close relationship between the two substances, and suggest that probably quicklime, like magnesia, is the oxide of a metal.

67. Does Quicklime contain Oxygen ?—We have seen that a good way of testing for the presence of oxygen in compounds is to try the action of heated magnesium upon them. Let us see whether quicklime is acted upon when treated thus.

Ex. 67.—Powder 6 or 8 gm. of quicklime and mix it with an equal bulk of magnesium filings. Put the mixture into a hard glass test-tube and pack it in tightly by pressing it down with a pencil or glass rod. Have ready a cork that fits the tube. Now heat the mixture in the Bunsen flame. After a little the mass will glow brightly, showing that chemical action is taking place, and heat is being evolved. As soon as the glow stops cork the tube tightly and leave it to cool.

The fact that there is a violent action when quicklime and magnesium are heated together does not, of course, *prove* that quicklime is not an element—far less does it prove that quicklime contains oxygen. To do this we should have to prove that magnesium oxide is formed by the action. Unfortunately it is not easy to do this, for the magnesium oxide is mixed with the other substance that is formed at the same time, and probably also with some unchanged quicklime. But if on cooling you put the powder into water, you will find that there is a brisk effervescence and *hydrogen* is evolved. Now we have seen that at least two metals (sodium and potassium) have the power of decomposing water at the ordinary temperature, setting free hydrogen and forming a soluble "alkaline"[2] substance which must contain the metal and oxygen. The most probable conclusion, then, is that quicklime is a compound of a metal (calcium) with oxygen; that when it is heated with magnesium we get magnesium oxide and the metal; and that when the metal is thrown into water it sets

[1] Should time permit, Ex. 53 may be repeated, using magnesite instead of chalk. This substance may be decomposed completely by heating in an ordinary porcelain crucible. But in Ex. 54 it would be necessary to use heat.

[2] Alkaline substances are those that have the property of turning reddened litmus blue and of neutralising acids.

free the hydrogen and combines with the oxygen of the water, forming quicklime once more, which in presence of sufficient water would, of course, form slaked lime. That this is actually what takes place has been proved by other experiments. We may now give to quicklime its chemical name of **calcium oxide.** By its union with water we get **calcium hydrate,** and by the action of carbon dioxide on either of these we get chalk or calcium carbonate.

68. Acid-forming Oxides and Basic Oxides.—It is interesting to notice how oxygen seems to play the part of go-between to the calcium and the carbon—the two other elements contained in the chalk. Calcium and carbon do not readily combine together, but each combines eagerly with oxygen; and the two oxides, as we have seen, readily combine together to form chalk. Carbon, as we know, forms by combining with oxygen a gas which has acid properties. Calcium, on the other hand, forms an oxide (quicklime) which has the reverse of acid properties, turns blue again litmus that has been reddened by an acid, and neutralises acids, combining with them to form neutral salt-like substances which are soluble in water and have no action on litmus, and neither dissolve metals like the acids nor combine with acids like quicklime. We shall find that these two compounds, calcium oxide and carbon dioxide, are typical of many others which will be studied later on. Oxides which behave like quicklime are known as "basic oxides" or **bases.** We shall find that most of the oxides formed by metals belong to this class. Most of the non-metallic elements on the other hand, such as carbon, sulphur, phosphorus, and nitrogen, form oxides which belong to the opposite class of **acid-forming oxides,** of which carbon dioxide is an example.

The name *anhydride* (literally "without water") is often given to the oxides of the latter class, referring to the fact that they combine with water to form acids.

QUESTIONS AND EXAMPLES ON CHAPTER VIII.

1. By what experiments could you prove that carbon dioxide contains carbon and oxygen? Give an analytical and also a synthetical method.

2. The density of carbon dioxide is 22. Calculate the weight of 20 litres of the gas at N.T.P.

3. If 1·48 gm. of slaked lime be heated in a crucible, what weight of quicklime will be left?

4. What weight of chalk could be got from 1·48 gm. of slaked lime by the action of carbon dioxide?

5. Is chalk a mixture or a pure substance? Give reasons for your answer.

6. When a candle is burned in a bottle of air, and lime water is then poured into the bottle, a precipitate of chalk is formed. What does this tell us as to the composition of the candle?

7. How would you test an unknown gas to find out whether it contained free (*i.e.* uncombined) oxygen? Suppose that this were found to be absent, how would you test for the presence of oxygen in the combined state?

8. Describe experiments which bring out the resemblance between lime and magnesia. To what class of oxides does each of these substances belong?

9. What is a hydrate? Give examples, and state what usually happens when the hydrate of a metal is strongly heated.

10. Explain fully the reasons for believing that when chalk is heated it gives off 44% of its weight of carbon dioxide gas.

CHAPTER IX

THE PROPORTIONS IN WHICH THE ELEMENTS COMBINE

69. Combination in fixed Proportions.—In the last two chapters we have studied the composition of several chemical compounds, and in every case we have found that the first law of chemical combination—viz. that substances combine in fixed and definite proportions by weight—holds good. We have next to find out whether the proportions in which the different elements combine with each other follow any simple general law; or whether the composition of every compound appears to be fixed without reference to that of others. For example, we have seen that mercury combines with oxygen and also with sulphur. Do the different weights of sulphur and oxygen which combine with a fixed weight of mercury also combine with each other, or is there no such simple relation? To carry out the necessary experiments with these three elements would be too difficult for beginners. We shall therefore choose the three elements, magnesium, oxygen, and hydrogen. We have already seen that hydrogen and oxygen combine in the proportion of 1 to 8. There is no difficulty in determining the proportions in which magnesium and oxygen combine. Magnesium and hydrogen unfortunately do not combine with each other; but we have seen that magnesium displaces hydrogen from acids, and we can find out whether the weight of hydrogen thus displaced by a given weight of magnesium bears any simple proportion to the weight of oxygen which would combine with that weight of magnesium.

70. Magnesium and Oxygen.—Ex. 68.—Weigh a porcelain crucible with its lid. Put into it about 20 cm. of magnesium ribbon previously cleaned with sand-paper. Weigh again to find the weight of magnesium taken. Place the crucible on a triangle, cover it, and heat strongly by the Bunsen

flame. Lift the lid slightly at intervals of 20 seconds or so to admit air, replacing it quickly so as to avoid the escape of any of the oxide. When the magnesium no longer glows on opening the crucible, remove the lid and continue to heat for ten minutes. Allow to cool, and weigh. After weighing, moisten the oxide with 2 or 3 drops of water. Heat gently, and notice whether any smell of ammonia is given off. If so, the magnesia contains magnesium nitride, formed by the action of the nitrogen of the air upon the heated metal. In this case the oxide must be dried slowly and then ignited. This treatment will convert the nitride into the oxide, which can then be weighed. Now calculate the weight of magnesium which combines with 8 gm. of oxygen. If this experiment is carefully done, you will find that 8 gm. of oxygen combines with almost exactly 12 gm. of magnesium to form magnesia. We already know that 8 gm. of oxygen combine with 1 gm. of hydrogen to form water. It may be said, then, that 12 gm. of magnesium are *equivalent* to 1 gm. of hydrogen, since either will combine with 8 gm. of oxygen, just as we may say that 12 pence are equivalent to 48 farthings, since we can exchange either of them for 1 shilling.

71. Magnesium and Hydrogen.—Let us next make an experiment to find out what weight of magnesium is required to set free 1 gm. of hydrogen from an acid.

Ex. 69.—Fit up the apparatus shown in Fig. 42. In the small flask put about 40 c.c. of dilute hydrochloric or sulphuric [1] acid (1 volume of strong acid to 3 volumes of water). The rest of the apparatus is exactly the same as that already used in Experiment 60, and is connected with the small flask by 2 or 3 inches of india-rubber tubing. Fill the large bottle and the delivery tube with water, and close the latter by a clip, as in Experiment 60. Now weigh out 0·2 to 0·3 gm. of clean magnesium wire. Roll it up into a small bundle and slip it into the neck of the small flask, which must be held nearly horizontal so that the magnesium remains in the neck and does not come into contact with the acid. Now put in the

[1] Some pupils should take hydrochloric acid, others sulphuric acid, and the question whether the volume of the hydrogen depends on which acid is used should be discussed afterwards in the light of the results.

cork tightly, tilt the flask so that the magnesium falls into the acid, open the clip, and collect in a jar the water which is expelled by the hydrogen. When all the magnesium has dissolved, immerse the little flask in a beaker of water at the temperature of the laboratory. Leave the apparatus for 10 minutes to allow the hydrogen to cool. Raise the jar till the level of the water is the same in it as in the large bottle. Wait a minute or two and close the clip. Measure the water in the jar, which gives you the volume of the moist hydrogen at the temperature and pressure of the laboratory. In order to calculate its weight we must know what the volume would become when the gas is dry and at N.T.P. This may either be found by calculation or by comparison with a standard volume of gas.

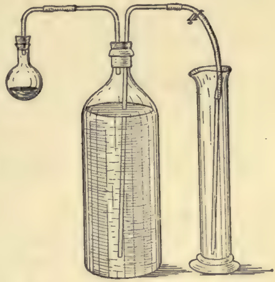


Fig. 42. — Apparatus for finding the volume of hydrogen set free by a given weight of a metal.

NOTE FOR THE TEACHER.—A convenient instrument for this purpose may be made as follows :—Take a piece of glass tubing, 35 cm. long and with a uniform bore of 2 mm. Breathe through it so as to moisten the sides ; then seal one end in the Bunsen flame. Introduce a small funnel, made by drawing out an ordinary test-tube (see Appendix, p. 180) into the other end, and through this pour in a few drops of mercury, sufficient to fill 3 or 4 cm. of the tube. The thread of mercury should be near the open end of the tube. Now calculate what would be the volume of 10 c.c. of dry air at N.T.P. if raised to the temperature and pressure of the laboratory and saturated with water vapour. Suppose you find that it would become 10·35 c.c. ; then if we adjust the thread of mercury so as to enclose a column of moist air 10·35 inches long, we shall know that this volume would contract to 10 inches when dry and at N.T.P. Pass through the mercury a capillary glass tube, made by heating a piece of ordinary tubing and removing it from the flame and quickly drawing the ends apart. This will allow the air in the closed tube to communicate with the atmosphere. Tilt the tube slightly up or down as required, till the column of air measures exactly 10·35 inches, then withdraw the capillary tube ; close the mouth of the tube loosely by a tiny plug of cotton wool, and the "volumeter" is complete. It may

conveniently be mounted horizontally on a board and furnished with a scale from 1·00 (corresponding to 10 inches) to 1·30 (corresponding to 13 inches) by tenths of an inch. Then the observed volume of gas in any experiment has only to be divided

Fig. 43.—Volumeter for finding quickly and easily the correction to be applied in order to reduce an observed volume of gas to the volume it would occupy when dry and at normal temperature and pressure.

by the reading of the scale in order to find what would be its volume when dried and reduced to N.T.P.

An actual experiment gave the following figures :—

Weight of magnesium wire	=	·240 gm.
Volume of hydrogen	=	229·5 c.c.
Reading of volumeter	=	1·035

$$\therefore \text{ Volume of hydrogen at N.T.P.} = \frac{229{\cdot}5}{1{\cdot}035} = 221{\cdot}8 \text{ c.c.}$$

Since 1 litre of hydrogen at N.T.P. weighs ·09 gms.

The weight of this volume of hydrogen will be $\dfrac{221{\cdot}8 \times {\cdot}09}{1000}$

$= {\cdot}01996$ gm.

or almost exactly ·02 gm.

i.e. ·24. gm. of magnesium gives ·02 of hydrogen, or it would require 12 gm. of magnesium to set free 1 gm. of hydrogen.

72. Equivalents.—This result may be confirmed in a more direct manner by using the method already employed in Ex. 54, where we found the percentage of carbon dioxide in chalk by mixing weighed quantities of chalk and acid and determining the loss in weight caused by the evolution of the gas. Hydrogen is so light that this method does not give very exact results when used for it, but the relation shown by the last experiment is so important that it is worth while to confirm it by an independent experiment.

Ex. 70.—Fit up the apparatus shown in Fig. 44. *A* and *B*

are test-tubes each of about 20 c.c. capacity. Into *B* put 10 c.c. of distilled water, and into *A* about 10 c.c. of strong sulphuric acid. The tube *C* is closed by a stopper made from an inch of rubber tubing and a short piece of glass rod. *D*, through which the hydrogen escapes after being dried by passing through the sulphuric acid in *A*, is loosely closed by a small plug of glass wool. Put into *B* about 0·3 gm. of clean magnesium wire accurately weighed. Allow the apparatus to cool thoroughly and weigh it as accurately as possible, hanging it to the hook of the balance by the wire shown in the figure. Now attach to *D* a piece of rubber tubing, and to that a tube filled with small pieces of calcium chloride and having a short piece of rubber tubing attached to its other end. Suck some air through this tube (the calcium chloride tube is to prevent moisture from the breath passing into the apparatus). This will cause a partial vacuum in *B*, and when the suction is stopped one or two drops of sulphuric acid will be forced back from *A* into *B*. Hydrogen is then given off, and is dried by passing through the sulphuric acid in *A*. When the action slackens more air is sucked out, and this is repeated at intervals until all the metal has disappeared. If at any time too much acid is allowed to pass into *B*, and the liquid consequently becomes hot, it should be cooled by dipping *B* into a beaker of cold water. (The cork should not be wetted.) The stopper is now removed from *C*, and air, dried by passing through a calcium chloride tube, is drawn through the apparatus to expel the remaining hydrogen. Lastly, the stopper is replaced, the apparatus is allowed to cool completely, and is again weighed. The loss in weight as compared with the first weighing gives, of course, the weight of hydrogen set free by the magnesium from the acid.

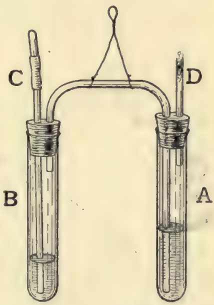
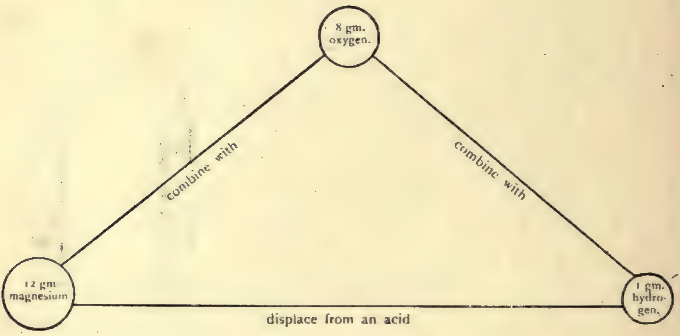


Fig. 44.—Apparatus for finding what weight of hydrogen is set free from an acid by a known weight of magnesium.

In an actual experiment with this apparatus:

0·272 gm. of magnesium set free 0·022 gm. of hydrogen
or, 12 gm. of magnesium set free 0·98 gm. of hydrogen—

a very close approximation to the result of the last experiment, according to which 12 gm. of magnesium give 1 gm. of hydrogen. But we have seen from Ex. 68 that 12 gm. of magnesium combine with 8 gm. of oxygen to form magnesia. It appears, then, that the *weight of magnesium which sets free* 1 *gm. of hydrogen is also that which combines with* 8 *gm. of oxygen: and these are the weights of hydrogen and oxygen which combine together to form water.* We may express this result by a diagram, thus:—



The diagram shows that for each of these three elements there is a number which expresses the proportion in which it combines with or replaces either of the others. This number is called the **equivalent** of the element. If we take the equivalent of hydrogen as equal to 1, then that of oxygen is 8, and that of magnesium is 12. We might, of course, choose any number we please for the equivalent of hydrogen. If, for example, we were to call it 100, then the equivalent of oxygen would be 800, and that of magnesium would be 1200.

73. Use of Symbols.—By adopting some kind of shorthand expression to stand for the equivalent weight of each element, we can express very shortly and conveniently the composition of their compounds. For example, suppose we agree that the symbol *Hy* shall stand for 1 part by weight of hydrogen, *Ox* for 8 parts by weight of oxygen, and *Ma* for 12 parts by weight of magnesium, then the composition of water would be given

by the expression *HyOx*, which would mean that 1 part by weight of hydrogen is united to 8 parts by weight of oxygen, forming 9 parts by weight of water. In the same way magnesium oxide would be represented by *MaOx*, which expresses the fact that in every 20 parts by weight of magnesium oxide, 12 parts by weight of magnesium are united with 8 parts by weight of oxygen. Such a shorthand expression for a fixed weight of a compound is called a **chemical formula**. The corresponding expression for the fixed weight of an element is called the **symbol** of the element. (The symbols and formulæ here given are not those actually in use by chemists, as will be explained later.)

74. Equivalents of other Elements. — Having fixed the equivalent weights of the three elements, magnesium, oxygen, and hydrogen, we can determine those of other elements by finding the proportion in which they combine with any of those three. For example, silver does not readily combine with either oxygen or hydrogen, but if we put magnesium into the solution made by dissolving silver in nitric acid and evaporating off the excess of acid, the magnesium takes the place of the silver in the solution, while the silver is precipitated as a glistening white powder. This is weighed, and the weight of silver precipitated by 12 parts by weight of magnesium is calculated. This weight is the equivalent of silver.

Ex. 71.—Carefully weigh a small porcelain basin and note its weight. Put into it 3 to 4 gm. of silver nitrate and dissolve this in 10 or 12 c.c. of distilled water. Now weigh very carefully 0·1 to 0·2 gm. of magnesium ribbon. Put the magnesium into the solution, and stir with a glass rod until none of the magnesium remains. Allow the precipitate to settle, and pour off the clear liquid on to a filter,[1] taking care to leave as much as possible of the silver precipitate in the basin. Now fill up the basin with distilled water. Stir, allow to settle, pour off the clear liquid through the filter, and repeat this process two or three times with distilled water, and finally once with methylated spirit. The filter must be allowed to

[1] The hardened filters made by Schleicher and Schüll are very suitable for these experiments, as the precipitate can be almost completely removed from the paper after drying.

empty itself before each fresh washing is poured in. Now heat both basin and filter[1] in the air-bath till quite dry. Brush the powder from the filter into the basin as completely as possible and find its weight. Calculate how many gms. of silver would have been precipitated by 12 gm. of magnesium. It will be found that 108 parts by weight of silver are equivalent to 12 of magnesium, and consequently to 8 of oxygen or 1 of hydrogen.

We shall next take the case of the element tin. We have already seen that this metal dissolves in strong hydrochloric acid with the evolution of hydrogen. Its equivalent to hydrogen may be determined exactly as was done with magnesium in Ex. 69, except that strong hydrochloric acid must be used in the small flask. It will be found that about 59 parts by weight of tin are required to set free 1 part by weight of hydrogen.

But tin also readily combines with oxygen. When heated in the air it is difficult to convert the whole of the tin into oxide, unless the experiment is continued for a very long time. It is better to convert the tin into oxide by the use of some oxidising agent. Nitric acid is most convenient. As we have seen, this acid converts most metals into soluble crystalline salts called nitrates. These nitrates, when heated, usually give off red fumes (consisting of compounds of oxygen and nitrogen) and leave behind a residue of the oxide of the metal. (What do you infer as to the composition of nitric acid?) In the case of tin the action is different. No nitrate is formed, but the tin is converted into an insoluble white hydrate, which, when heated, behaves exactly like slaked lime or calcium hydrate—*i.e.* it loses water, and leaves behind the oxide of the metal.

Ex. 72.—Weigh out about 0·5 gm. of *pure*[2] tinfoil into a porcelain crucible, which has been previously weighed along with its lid. Cover the crucible with a watch glass. Dip a pipette into strong nitric acid, raise the watch glass a little and allow 2 or 3 drops of the acid to run into the crucible. Wait till the effervescence caused by the action of the acid on the metal has ceased, and repeat the process until a further addition of acid produces no change, showing that all the tin has been acted upon. Now put the crucible on a sheet of

[1] The filter should be removed from the funnel and opened out—otherwise it will take a long time to dry.

[2] Commercial tinfoil generally contains lead and copper.

asbestos cardboard heated by a small flame. Remove the watch glass, first washing off into the crucible by means of *a few drops* of water from the wash bottle any white particles of tin hydrate which may adhere to it. Stir the contents of the crucible with a very small glass rod and continue to heat gently, with occasional stirring, until they form a dry yellowish powder and no smell of nitric acid can be detected. Scrape off into the crucible by means of a knife any of the powder which adheres to the glass rod, and finally cover the crucible with its lid and heat it as strongly as possible in the Bunsen flame for a quarter of an hour, allow it to cool, heat again for five minutes, and repeat this till the weight is constant. Calculate what weight of tin is required to combine with 8 parts by weight of oxygen.

75. Combining Weights and Symbols.—When the figures of the last two experiments are compared, you will find that they give a very remarkable result, for whereas 59 parts by weight of tin are required to set free 1 gm. of hydrogen, only half this amount, or 29·5 parts by weight, is required to combine with 8 parts by weight of oxygen. It appears, then, that tin has 2 equivalents, one of which is double the other. If we take T as the symbol for tin, we may decide to make it stand for either 29·5 parts by weight or 59 parts by weight, according as we choose the weight of tin which combines with 8 parts by weight of oxygen or that which sets free 1 part by weight of hydrogen. This uncertainty as to which number is to be taken as the equivalent does not in the least interfere with the expression of our results by formulæ. In the former case the formula of tin oxide would be written TOx where T equals 29·5 and Ox equals 8. In the latter case the formula would be written $T'Ox_2$ where $T' = 59$ and $Ox_2 = 8 \times 2 = 16$. The case of tin is a typical one; many other elements have more than one equivalent, but in every case the higher number is a simple multiple of the lower. The number actually chosen as the **combining weight** of any element is either the equivalent or some multiple of it. The choice of the actual number depends on theoretical considerations which do not concern us at present. The symbols in actual use are not exactly those which we have taken as examples. As a rule, the first or first and second letters of the Latin name of the element

are used. The following list gives the names, symbols, and combining weights of all the commoner elements.

Name.	Symbol.	Combining Weight or "Atomic Weight."
Aluminium	Al	27
Antimony (*Stibium*)	Sb	120
Argon	A	40
Arsenic	As	75
Barium	Ba	137
Bismuth	Bi	208
Boron	B	11
Bromine	Br	80
Cadmium	Cd	112
Calcium	Ca	40
Carbon	C	12
Chlorine	Cl	35·5
Chromium	Cr	52
Cobalt	Co	59
Copper (*Cuprum*)	Cu	63
Fluorine	F	19
Gold (*Aurum*)	Au	197
Hydrogen	H	1
Iodine	I	127
Iron (*Ferrum*)	Fe	56
Lead (*Plumbum*)	Pb	207
Magnesium	Mg	24
Manganese	Mn	55
Mercury (*Hydrargyrum*)	Hg	200
Nickel	Ni	58·7
Nitrogen	N	14
Oxygen	O	16
Phosphorus	P	31
Platinum	Pt	195
Potassium (*Kalium*)	K	39
Silver (*Argentum*)	Ag	108
Silicon	Si	28
Sodium (*Natrium*)	Na	23
Sulphur	S	32
Tin (*Stannum*)	Sn	118
Zinc	Zn	65

76. Equations.—On consulting the list we find, for example, that the symbol for tin is Sn (from stannum), and its combining weight 118, four times its equivalent to hydrogen. The symbol of oxygen is O, and its combining weight 16, or twice the equivalent. Since we have found that tin oxide contains 8 parts by weight of oxygen to 29·5 of tin, its formula is SnO_2. Its formation by heating tin in the air may be expressed in what is called a chemical equation, thus:

$$\begin{array}{ccccc} Sn & + & 2O & = & SnO_2. \\ 118 & + & \underbrace{2 \times 16}_{32} & = & \underbrace{118 + 32}_{150} \text{ parts by weight.} \end{array}$$

The sign = in such an equation is to be taken as meaning "give." It has not the same meaning as in Algebra. The equation expresses in the shortest possible form the facts brought out by experiment—namely, that when tin combines with oxygen, for every 118 parts by weight of tin, 32 parts by weight of oxygen are added on, forming 150 parts by weight of tin oxide. In the same way the formation of water by the union of oxygen and hydrogen is expressed by the equation

$$2H + O = H_2O$$

and that of magnesium oxide by

$$Mg + O = MgO$$

The action of magnesium on steam may be represented by

$$Mg + H_2O = MgO + 2H$$

as may readily be proved by repeating Ex. 39 with a weighed quantity of magnesium, when it will be found that for every 24 centigrammes of magnesium that are burned in the steam, 2 centigrammes of hydrogen are set free.

77. Calculations of Quantities from Equations. — When the equation for a reaction is known, it may be used to calculate the quantity of material required to give a certain weight of the product; or, *vice versâ*, to find how much of the product we may expect to get from a given quantity of the original substances. For example, we can calculate from the equation

$$Mg + H_2O = MgO + 2H$$

what weight of hydrogen could be got by burning a given weight of magnesium in steam, or what weight of magnesium would be required to furnish a given weight of hydrogen. Suppose we wish to know what weight of hydrogen could be got by the action of 5 gm. of magnesium on steam. We first consult the table of combining weights, and write under each symbol in the equation the number of parts by weight for which it stands. Thus:

$$\begin{array}{lllll} Mg + & H_2O & = & MgO & + \quad 2H \\ 24 + & (2+16) & = & (24+16) & + \quad 2 \text{ parts by weight} \\ 24 + & 18 & = & 40 & + \quad 2 \quad\quad ,, \end{array}$$

The question then becomes, "If 2 gm. of hydrogen can be got by burning 24 gm. of magnesium, how much can be got by burning 5 gm. of magnesium?" and the answer is found from the statement:—

$$\overbrace{24 : 5}^{\text{grammes of magnesium}} \quad :: \quad \overbrace{2 : x = \frac{2 \times 5}{24} = \cdot 417.}^{\text{grammes of hydrogen}}$$

If we wish to know what weight of magnesium is required to give 0·3 gm. of hydrogen, the statement will be:

$$\overbrace{2 : 0 \cdot 3}^{\text{grammes of hydrogen}} \quad :: \quad \overbrace{24 : x = 3 \cdot 6.}^{\text{grammes of magnesium}}$$

Since a litre of hydrogen at N.T.P. always weighs ·09 gm., we can also calculate what *volume* of hydrogen at N.T.P. can be got from given weights of magnesium or of water, and conversely what weights of magnesium and water are required to give a certain volume of hydrogen at N.T.P. A single example will suffice. Suppose we wish to know what weight of magnesium is required to give 100 litres of hydrogen at N.T.P. Since 1 litre of hydrogen at N.T.P. weighs ·09 gm., 100 litres will weigh $\cdot 09 \times 100 = 9$ gm. Then

$$\overbrace{2 : 9}^{\text{grammes of hydrogen}} \quad :: \quad \overbrace{24 : x.}^{\text{grammes of magnesium}}$$

which shows that 108 grammes of magnesium would be required.

78. Equations are merely Records of Experiments.—It must never be forgotten that in such calculations we are simply making use of the results of quantitative experiments previously made either by ourselves or by other experimenters. In other words, an equation is valueless unless we know that the reaction which it represents really takes place, and *that the proportions by weight have been verified by experiment.* For example, we know from Ex. 30 that iron and oxygen combine to form a compound called oxide of iron. But if we were to presume from this that the reaction can be represented by the equation $Fe + O = FeO$, and were then to proceed to calculate from this equation how much oxygen will combine with a given weight of iron, we should get entirely wrong results. For we have made no experiment to determine the proportions by weight of iron and oxygen in the compound. As a matter of fact, it does not contain 56 parts by weight of iron to 16 parts by weight of oxygen as implied by the formula FeO, but 56 parts by weight of iron to 21·33 parts by weight of oxygen, and its formula is therefore Fe_3O_4. Notice also that equations in themselves tell us nothing as to the conditions under which a chemical reaction occurs. For instance, the equation $2H + O = H_2O$ tells us merely that hydrogen and oxygen combine in the proportion of 2 parts by weight of hydrogen to 16 parts by weight of oxygen. It does not tell us that this combination takes place only at a high temperature, and that the two gases may be mixed at the ordinary temperature without the occurrence of any chemical action.

NOTE FOR THE TEACHER.—The following are a few additional experiments on equivalents which can be relied on to give accurate results, and are not too difficult for beginners.

Zinc.—The equivalent to hydrogen may be determined exactly as in Ex. 69. Use about ½ gm. of the metal in thin foil or sheet, and either dilute hydrochloric or sulphuric acid. The former acts more quickly. The equivalent may also be determined by using the metal to precipitate silver from silver nitrate, exactly as in the case of magnesium, or by conversion into oxide, as in the case of tin. The last method is more difficult to carry out than the others.

Aluminium.—The equivalent is best determined by measuring the hydrogen evolved when the metal is dissolved in dilute hydrochloric acid (equal volumes of strong acid and water). About

·2 gm. of thin foil or wire should be used. If the solution thus prepared be evaporated to dryness, with the addition of a few drops of nitric acid, the aluminium is completely converted into oxide, and thus from the same experiment two values for the equivalent can be got.

Iron.—This metal is treated exactly like aluminium. Care must be taken, however, to fill the large bottle completely with water so as to leave as little air in the apparatus as possible, for the solution of ferrous chloride which is formed absorbs oxygen readily, and this would cause the volume of hydrogen to appear smaller, and the equivalent of the metal, therefore, larger than the actual number. About ½ gm. of thin wire (florist's wire) may be used, and it should be carefully cleaned with emery paper before weighing.

Sodium.—The equivalent may be determined by repeating Ex. 40, with a weighed quantity of metal (about 0·2 gm.). The metal should be cut in the form of a long, thin bar, weighed as quickly as possible, and then either packed into a piece of lead tube, closed at one end, or wrapped tightly round with several thicknesses of stout lead foil, leaving only a narrow opening at one end for the entrance of the water. The little bundle is then put *quickly* under a narrow jar filled with water, and standing mouth downwards in the pneumatic trough. The hydrogen is collected in the jar, and its volume found in the usual way.

Copper.—This metal does not set free hydrogen from acids, but its equivalent may be determined in several ways. It may be used to precipitate silver from silver nitrate solution, as in Ex. 71. In this case the solution of silver nitrate should be hot. About ½ gm. of copper in thin foil may be used. Copper may itself be precipitated from a solution of copper sulphate by weighed quantities of zinc or iron (not by magnesium, although this experiment was once prescribed in an examination by an examiner who had not tried it). About 1 gm. of thin iron wire or zinc foil may be used. The precipitated copper oxidises readily. It should be washed with alcohol, and then dried as quickly as possible at a temperature of not more than 100° C. The equivalent of copper may also be found by reducing a known weight of the pure oxide in a stream of hydrogen or coal-gas (Ex. 49), or conversely by oxidising a known weight of the metal with nitric acid, as in the case of tin. The last experiment, though often recommended, is not very suitable for young students, as the tendency to loss by spurting makes it difficult to get good results.

QUESTIONS AND EXAMPLES ON CHAPTER IX.

1. State exactly what is meant by the statement that the equivalent of chlorine is 35·5.

2. Give an example of an element which has two different equivalents. What relation is found between the values of the two equivalents in such cases?

3. If 2 gm. of mercury combines with ·71 gm. of chlorine, what is the equivalent of mercury?

4. Find the equivalent of a metal from the following numbers:—Weight of metal used, ·453 gm.; volume of hydrogen obtained, 194·5 c.c.; volumeter reading, 1·040.

5. Calculate what would be the reading of the volumeter when the barometer stands at 747 mm. and the thermometer at 15° C. (Vapour tension of water at 15° C. = 13 mm. of mercury.)

6. Assuming the equation $3Fe + 4H_2O = Fe_3O_4 + 8H$ to be correct, calculate the weight of iron required to furnish 10 litres of hydrogen at N.T.P. What weight of oxide of iron would be left behind?

7. When mercury is heated with sulphur (Ex. 1) the compound formed contains 86·2 % of mercury and 13·8 % of sulphur. Find its formula.

8. Silver nitrate has the formula $AgNO_3$. Find what weight of silver should be left behind on heating 1·70 gm. of silver nitrate.

9. Air is sometimes represented by the formula N_4O. Why is this incorrect?

10. When phosphorus burns in oxygen the compound formed has the formula P_2O_5. Calculate the weight of oxygen that combines with 31 gm. of phosphorus.

11. When pure oxide of copper is heated in hydrogen (p. 67) 26·3 gm. of copper oxide is reduced for every 6 gm. of water produced. Write the equation for the reaction.

12. From the numbers given on page 80 write the equation for the reaction that takes place when carbon burns in oxygen.

CHAPTER X

SALT AND HYDROCHLORIC ACID

79. Common Salt.—We shall next turn our attention to a substance which is almost as common as chalk, and is of even greater importance—common salt. This substance is present in enormous quantities in sea-water, from which it can be got by evaporation, and it also occurs in certain localities as a mineral, to which the distinctive name of rock salt is given.

Ex. 73.—Examine a piece of rock salt. Note its transparency, its brownish colour (is this equally diffused throughout the mass?), its solubility. Allow a few drops of the solution to evaporate on a watch-glass, and examine with the aid of a lens the crystals that are formed. Break a piece with a hammer and note the pronounced cleavage. What is the angle between the broken faces? Powder a little and heat some of it on a small loop of thin platinum or iron wire in the Bunsen flame. What happens? Heat a little of the powder in a dry tube and note whether anything happens. Write an account of your observations.

Since heat produces no chemical change on salt, we shall next try the action of sulphuric acid upon it.

Ex. 74.—Put a gramme or two of salt into a test-tube, add a little sulphuric acid, and heat gently. What happens? Fit a leading tube to the test-tube and try to collect the gas by downward displacement in another *dry* test-tube. Close the latter with the thumb and put it mouth downwards into water. What happens? What is the action of the gas upon litmus? Can it be collected over water?

For preparing a larger quantity of the gas from salt and sulphuric acid, the apparatus shown in the figure may be used. The experiment of filling a jar with the gas and opening it under water should be repeated and the action of the gas upon a lighted taper should be tried. The density

of the gas may also be determined by the method already used for oxygen, care being taken that the whole apparatus is perfectly dry.[1]

Ex. 75.—Using the apparatus shown in Fig. 45, heat some coarsely powdered rock salt with strong sulphuric acid and pass the gas into a weighed test-tube containing 5 c.c. of cold water. The tube delivering the gas must not touch the water. Continue to pass in the gas until no more seems to dissolve in the water. Note that the water gets hot and that its volume increases. Weigh the tube containing the liquid and find what weight of gas has been dissolved by the 5 gm. of water. Examine the liquid. Note its smell, its action on litmus and on metals. What is it?

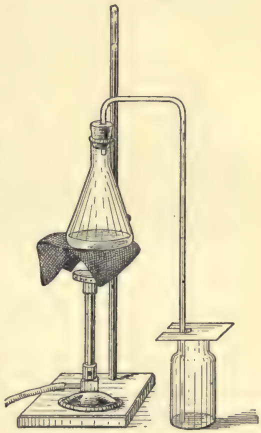


Fig. 45.

80. Hydrochloric Acid.—The liquid prepared in the last experiment is what is usually called hydrochloric acid. The experiment shows that it is made by dissolving the fuming gas from salt in about twice its own weight of water. This is the ordinary method of preparing hydrochloric acid and is referred to in the old-fashioned name "spirit of salt," which is still sometimes given to the acid.

We have next to ask ourselves what is the composition of the gas. We have seen that the liquid acid, when treated with metals, gives hydrogen, but this hydrogen may come from the water used when preparing it. If it comes from the gas, then we should be able to get hydrogen from the gas by heating metals in it. Let us try an experiment to find out whether this is the case or not.

Ex. 76 (*Teacher only*). — Fit up the apparatus shown in Fig. 46. Close the end of the delivery tube by a Bunsen valve.[2] See that the whole apparatus, including the leading

[1] See note on p. 18 for method of drying.

[2] This is made as follows :—Cut off about 4 cm. of narrow black rubber tubing, having fairly thick walls. Put into it a small piece of wood—a

tube, is quite dry. Put into the flask, which should be supported on a piece of asbestos cardboard, about 20 gm. of roughly powdered rock salt, and pour on to it about 20 c.c. of strong sulphuric acid. Fit the cork carrying the leading tube and an ordinary test-tube into the neck of the flask, and place the end of the leading tube under water in the pneumatic trough. The air in the apparatus will soon be expelled and the bubbles of hydrochloric acid will dissolve completely as they escape into the water. While this is going on weigh a hard glass test-tube[1] (which must fit the same cork as the other test-tube), put into it about ·2 gm. of clean sodium and weigh again. Now remove the test tube from the apparatus and quickly substitute the hard glass tube containing the sodium. Heat the flask to get a brisk current of gas. Wait till the air in the test-tube has been completely expelled and then place a jar filled with water over the delivery tube and heat the sodium strongly till it begins to glow. (This may require the blow-pipe flame.) Collect the gas which is evolved. Measure it and calculate its volume at N.T.P. Test it to make sure that it is hydrogen and then calculate its weight. Weigh also the test-tube after replacing the gas it contains by air and find the increase in its weight.

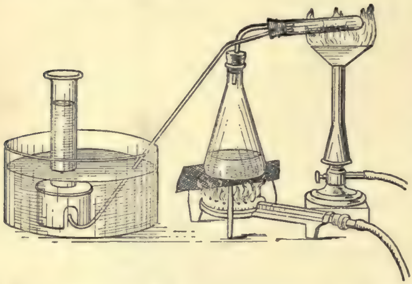


Fig. 46.—Analysis of hydrochloric acid gas by means of sodium.

81. Composition of Salt.—The preceding experiment proves

match will do—and with a *sharp* knife, previously wetted, cut a slit about 1 to $1\frac{1}{2}$ cm. long through one side. Withdraw the wood. Close the end by a short piece of glass rod and the valve is complete. Test it by trying to suck air into the mouth through it. You will find that the walls of the slit close tightly and no air passes in, although air *blown* into the tube passes out quite freely.

[1] For this and similar experiments the Jena glass combustion tubing is specially recommended as being much less liable to crack than ordinary combustion tubing.

clearly that the gas from salt contains hydrogen; and by comparing the weight of the hydrogen which is given off with the increase in the weight of the tube containing the sodium, we can find approximately the proportion between the weight of this hydrogen and that of the other element (or elements?) with which it is combined. In an actual experiment the increase in the weight of the tube was ·310 gm. and the volume of hydrogen at N.T.P. 98·1 c.c. = ·00883 gm. or 1 gm. of hydrogen had been combined with 35·1 gm. of the other element.

Let us next examine the compound left in the tube. It is a white solid which dissolves in water, and on evaporation gives cubical crystals. Compare these with the crystals you obtained in Ex. 73.—Crush some with the blade of a knife and heat them on a clean platinum (or iron) wire in the Bunsen flame. Taste a drop of the mother-liquor. The white solid obtained by the action of hydrochloric acid on sodium is common salt, which must therefore be a compound of sodium with another element which in hydrochloric acid is united to hydrogen.

In this experiment some of the sodium acts upon the glass, and the results do not therefore give the ratio between the weights of sodium and salt with accuracy. This ratio can be found as follows:—

Ex. 77.—Weigh a small porcelain basin. Put into it about 5 c.c. of strong hydrochloric acid. Now weigh out, as accurately as possible, about ·2 gm. of sodium. Cover the basin with a watch-glass, cut the sodium into small pieces and put these, one at a time, into the acid. When all the sodium has been added rinse the watch-glass into the basin with a few drops of distilled water from the wash-bottle, evaporate to dryness on the water-bath, and heat the basin in the air-bath till its weight is constant. Find what weight of common salt would be formed from 23 gm. of sodium, and hence the weight of the new element which combines with 23 parts by weight of sodium.

82. Separation of the other Element contained in Salt.—Our next task must be to obtain this element (if such it be) in the pure state. Neither salt nor hydrochloric acid is broken up into its elements by heat, or at least by any heat that we can conveniently apply. We must therefore look for some means of setting free the element by chemical action. To do this we

must act on hydrochloric acid gas with some substance which will combine with the hydrogen and not with the other element. Now the only element which we have found to combine readily with hydrogen is oxygen. Free oxygen has no action on hydrochloric acid except at a very high temperature; but there are many compounds containing what may be called loosely combined oxygen which will serve our purpose. Potassium chlorate is one of these.

Ex. 78.[1]—Put into a wide test-tube 2 or 3 c.c. of strong hydrochloric acid. Add half its volume of water and drop in a crystal of potassium chlorate. Heat gently. Describe the appearance of the gas which is given off. Is it heavy or light? Put into it a piece of moistened litmus paper on the end of a glass rod. What happens? Notice the smell of the diluted gas. (This must be done cautiously, and great care must be taken not to breathe the gas.) Find out also whether the gas is soluble in water. The heavy green gas obtained in this experiment is the element of which we are in search, and which is combined with hydrogen in hydrochloric acid, and with sodium in common salt. It has been named chlorine from the Greek *chlōros*, green.

83. Preparation of Chlorine.—The gas prepared by the action of potassium chlorate on hydrochloric acid is mixed with a small quantity of another gas, a compound of chlorine and oxygen. Chlorine can be prepared in many other ways, but all those in common use depend on the same principle—hydrochloric acid is acted upon by an oxidising agent, the oxygen combines with the hydrogen to form water, and the chlorine is set free. The oxidising agent generally used is manganese dioxide, the same substance which we have already used in the preparation of oxygen. You will remember that in that experiment it does not give up any of its oxygen; but it can be made to do so by heating it more strongly, and in many experiments it acts as an oxidising agent. In this case the action is expressed by the equation—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl$$

(Find out from the table of combining weights the proportions

[1] All experiments with chlorine should be performed, if possible, in a special fume chamber with a good draught.

by weight represented by this equation, and suggest an experiment by which we might find out whether the equation correctly represents the facts.)

It will be seen that only half of the chlorine of the hydrochloric acid is set free, the other half remaining combined with the manganese to form a salt called manganese chloride, which can be got in pink crystals by evaporating the solution which is left behind.

84. Properties of Chlorine.—We shall next make a few experiments to show the chief properties of the new element, beginning with its action on hydrogen.

Ex. 79.—Prepare hydrogen from zinc and hydrochloric acid, as in Ex. 47, and connect to the flask by a few inches of rubber tubing a tube drawn out to a jet, and bent upwards at the end in the form of a J. Now fill a wide test-tube with chlorine, as in the last experiment. Make sure that all air is expelled from the hydrogen apparatus. Light the hydrogen at the jet, and plunge it into the tube of chlorine. Describe what happens. What evidence have you that hydrochloric acid is formed?

The action that takes place in this experiment is represented by the equation—

$$H + Cl = HCl.$$

(Look up the table of combining weights, and see whether this equation agrees with your result obtained in Ex. 76, for the composition of hydrochloric acid gas.)

Ex. 80.—Repeat the last experiment, using a jet of coal-gas instead of hydrogen. What differences and resemblances do you notice, and how do you account for them, remembering that coal-gas is a mixture of hydrogen with compounds of hydrogen and carbon?

Ex. 81.—Fill another wide test-tube with chlorine. Moisten a narrow strip of filter paper with one drop of turpentine or oil of lemon, and plunge it into the gas. It takes fire spontaneously. What products are formed?

Ex. 82.—Fill another tube with chlorine. Cut a narrow strip of copper foil, heat it in the Bunsen flame, and plunge it quickly in the gas. Examine the chloride which is produced. Try the same experiment with a red-hot iron wire.

The foregoing experiments bring out the most important

properties of chlorine—its tendency to combine with hydrogen whether the latter is in the free state or in combination with other elements; its readiness to combine with metals forming compounds called chlorides, and its bleaching action on vegetable colours. Notice that when any compound of hydrogen and carbon burns in chlorine the hydrogen only enters into combination. The carbon is always set free as soot.

85. Synthesis of Hydrochloric Acid from its Elements.—We are now in a position to confirm the results of Ex. 76 by undertaking the synthesis of hydrochloric acid gas from its elements. The experiment has special difficulties, because chlorine cannot be accurately measured over water owing to its solubility; and we cannot use mercury, as in the synthesis of water, because like most other metals it is attacked by chlorine.

Ex. 83 (*Teacher only*).—Procure the apparatus shown in Fig. 47. It consists of a tube, closed at each end by a glass stopper and divided at about one-third of its length by a stop-cock. Dry the tube thoroughly and see that the stoppers

Fig. 47.

and stop-cock fit tightly and are slightly greased with vaseline. Close the stop-cock and fill the smaller division of the tube with dry chlorine by downward displacement. The chlorine is made by heating manganese dioxide (or, better, crystals of potassium permanganate) with dilute hydrochloric acid (equal volumes of strong acid and water). The gas is passed first through a test-tube containing a little water, and then through another containing strong sulphuric acid. The first removes any hydrochloric acid gas that may be mixed with the chlorine, and the second frees it from water vapour. After passing through the sulphuric acid the chlorine is led into a large wide-mouthed bottle, at the bottom of which a layer of slaked lime has been placed. This absorbs the gas, forming a peculiar compound called bleaching powder,[1] and prevents it from escaping into the laboratory and causing a nuisance. After waiting ten minutes or so the chlorine is

[1] This should be examined afterwards and the action of acids upon it should be tried.

passed into the stoppered tube for several minutes. The delivery tube is then withdrawn and the stopper instantly inserted. The longer limb of the tube is filled in a similar way with dry hydrogen by upward displacement. Now open the stop-cock and put the tube away in a dark cupboard till the next lesson. It will be found on examination that the chlorine and hydrogen are now equally diffused throughout the tube, but that there is no indication that they have combined. Now leave the tube exposed to daylight (not direct sunlight) for some hours. The green colour of the chlorine will now be found to have disappeared entirely, showing that it has been completely converted into colourless hydrochloric acid gas. Put the mouth of the tube under mercury in a basin or mortar and remove the stopper. The mercury does not rise and no gas escapes, showing that no alteration in the volume of the gas has taken place. Now pour some water on to the surface of the mercury, and raise the mouth of the tube until it reaches the water, which will at once rise in the tube as it dissolves the hydrochloric acid gas. Find out the volume of gas that remains; test it to make sure that it is hydrogen, and find out also the capacity of each limb of the tube. Subtract the volume of the hydrogen left over from that originally taken, and thus find the proportion by volume between the hydrogen and the chlorine that have entered into combination. The experiment may be repeated with the proportions between the hydrogen and chlorine reversed. In this case it gives less accurate results owing to the solubility of chlorine in water, and the preliminary opening of the tube under mercury must be omitted.

This experiment shows that hydrochloric acid gas is made up of equal volumes of hydrogen and chlorine. Since the relative density of chlorine is found by experiment to be 35·5, it follows that the proportion by weight between the two gases is 35·5 to 1, the same that we have already obtained by the action of sodium on the gas.

86. Chemical Action of Light.—The action of light in bringing about the union of the hydrogen and chlorine in the last experiment is particularly interesting. Small bulbs of thin glass, which have been filled with a mixture of equal volumes of hydrogen and chlorine

(produced by the electrolysis of the acid—see page 113), can be bought and used to show the effect of a bright light in causing sudden combination between the two gases. When one of these bulbs is exposed to the light given out by magnesium wire, burning at a distance of a few inches, it bursts with a loud report, forming clouds of hydrochloric acid fumes. The experiment may also be carried out in a test-tube, which may be first half-filled with chlorine over hot water, then filled up with hydrogen, corked, and exposed to light as above. In this case, as the test-tube is made of somewhat thicker glass, the fragments of which might do mischief, it is well to cover it with a bell-jar.

87. Nature of an Explosion.—These experiments with hydrogen and chlorine bring out very well the nature of an explosion. When the gases combine slowly, as in Ex. 83, there is no perceptible evolution of heat. Nevertheless it can be shown, by suitable means, that a large quantity of heat is really produced; but it is evolved so slowly that it is conducted away through the glass of the tube as fast as it is produced. But when a flame is applied to the mixed gases, or when they are exposed to a very bright light, combination is almost instantaneous. The same quantity of heat is produced, but this time in a fraction of a second. Consequently the hydrochloric acid gas which is formed is heated to a very high temperature, and therefore expanded to many times its original volume, and it is this *sudden* expansion which causes the noise and shock which we call an explosion. It will be remembered that when the hydrochloric acid gas becomes cold, its volume is exactly the same as that of the mixture of hydrogen and chlorine from which it was produced, so that in this case the evolution of heat is the *only* cause of explosion. The same is true in the case of a mixture of oxygen and hydrogen, where, as we have seen, the products of combustion when cold measure only $\frac{1}{1100}$th of the original volumes of the mixed gases. In many cases—*e.g.* those of gunpowder, nitro-glycerine, and other explosives—the explosive effect is brought about mainly by the sudden change of a solid body occupying a very small volume into a very bulky mixture of gases, and the action of heat in causing expansion is only a minor factor.

88. Analysis of Hydrochloric Acid Gas.—The fact that hydrochloric acid gas contains half its volume of hydrogen can be shown very simply by the following experiment:—

Ex. 84.—Take a long tube closed at one end, such as was used in Ex. 33. See that it is perfectly dry, and fill it with hydrochloric acid gas by downward displacement. Withdraw the delivery tube slowly, and when it reaches the mouth of

the tube close the latter quickly with the thumb. Now remove the thumb for an instant, and quickly pour in 5 c.c. of sodium amalgam.[1] Close the tube again instantly with the thumb, shake well for a minute or two, and then transfer the tube to a deep jar of water. The action that takes place is exactly the same as in Ex. 76, and on opening the tube the water rises and fills about half of it. Measure the volume of the hydrogen after adjusting the pressure. Find the volume of hydrochloric acid gas used by subtracting the volume of the mercury from the total capacity of the tube. It will be found to be double the volume of the hydrogen.

89. Electrolysis of Hydrochloric Acid.—The experiment of passing an electric current through a solution of hydrochloric acid is often shown as a proof of its composition. The apparatus used is like that shown in Fig. 36, except that electrodes of carbon are used instead of the platinum plates, which would be attached by the chlorine. Hydrogen is evolved at the kathode and chlorine at the anode, but the experiment is a very unsatisfactory one, and incapable of giving accurate quantitative results. (Can you suggest why?)

90. Action of Hydrochloric Acid on Chalk.—We are now in a position to go back and investigate more fully the change that occurs when hydrochloric acid acts upon chalk. We have already seen that in this action the whole of the carbon dioxide is given off, and that the substance left behind on evaporation is the same whether we use chalk itself or chalk that has been deprived of its carbon dioxide—*i.e.* quicklime. We may, therefore, simplify the inquiry by leaving out the carbon dioxide, and try to find out what happens when hydrochloric acid acts upon quicklime. It has been shown (page 86) that there are strong reasons for thinking that

[1] This should be made by the teacher only. About 200 c.c. of mercury is put into a porcelain basin and gently heated. 2 gm. of clean sodium is cut up into small pieces, and these are put into the mercury one at a time by sticking the point of a knife or skewer into them and pressing them quickly under the surface of the metal. The operation should be done in a fume-chamber, the hands being protected by gloves, and the face by the glass of the sliding door. After use the amalgam should be allowed to stand under water until no more hydrogen is evolved, when the mercury can be dried and returned to the original stock.

quicklime is an oxide. This is probable, not only on account of its close resemblance to magnesia, which we know to be an oxide, but also because on heating quicklime with magnesium a violent action takes place, and the residue decomposes water, setting free hydrogen. Now, when hydrochloric acid acts on quicklime, we have at least four elements present —hydrogen and chlorine in the hydrochloric acid, and oxygen and a metal (?) in the lime. Since no gas is given off during the action, it follows that neither oxygen nor hydrogen is set free. It seems probable, therefore, that either the solid compound left behind on evaporation contains all the four elements or that it contains only two, the metal and the chlorine, and that the hydrogen and oxygen unite to form water. The first supposition seems unlikely, for we have seen that when metals act on hydrochloric acid the whole of the hydrogen is expelled and the metal combines with the chlorine only. The second supposition cannot be tested so long as we use the ordinary hydrochloric acid solution in the experiment, for any water that may be formed mixes with the much larger quantity of water already present, and cannot therefore be observed. But there is no difficulty in repeating the experiment with dry hydrochloric acid gas instead of the solution, and in this case if any water is formed we shall be able to see and test it.

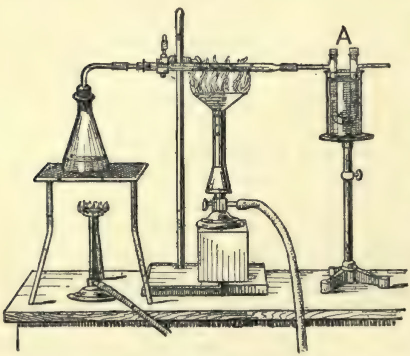


Fig. 48.

Ex. 85.—Fit up the apparatus shown in Fig. 48. Put into the hard glass tube sufficient quicklime in small lumps to fill loosely about 3 inches of the tube. This is strongly heated by the burner shown in the figure, and a *slow* current of hydrochloric acid gas is passed over it. A liquid collects in the tube *A*. When sufficient has collected, stop the experiment and examine the liquid.

It is clear that the liquid thus obtained is not pure water, for it turns blue litmus red, and causes effervescence when poured upon chalk. But if we remember the conditions of the experiment, we shall see that we could hardly expect to get pure water, but rather water containing hydrochloric acid in solution. It is easy to show that this is what we do get. We have only to add a little quicklime to the liquid, allow it to stand for a little, and then distil, in order to get from it perfectly pure water, which can be identified in any of the ordinary ways.

91. Proof that Quicklime contains Oxygen.—If we substitute chlorine for the hydrochloric acid gas in the last experiment, we obtain oxygen instead of water. The experiment may be carried out with exactly the same apparatus, except that a leading tube is substituted for the tube *A*. The oxygen is collected in the usual way, but instead of water the pneumatic trough is filled with a weak solution of caustic soda, which combines with any unchanged chlorine.

When this experiment is carried out with weighed quantities, it is found that 56 parts by weight of quicklime give 16 of oxygen and 111 of calcium chloride. The reaction is therefore expressed by the equation:

$$\begin{array}{l} CaO + 2Cl = CaCl_2 + O \\ 56 + 71 \text{ give } 111 + 16 \text{ parts by weight.} \end{array}$$

The action of hydrochloric acid gas on quicklime is in like manner represented by the equation,

$$\begin{array}{l} CaO + 2HCl = CaCl_2 + H_2O \\ 56 + 73 \text{ give } 111 + 18 \text{ parts by weight.} \end{array}$$

The last equation holds good whether the hydrochloric acid is used in the form of gas or as a solution in water, and this is true of most of the reactions in which hydrochloric acid takes part. We can now write the equation for the action of hydrochloric acid on chalk:

$$\begin{array}{l} CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O \\ 100 + 73 \text{ give } 111 + 44 + 18 \text{ parts by weight.} \end{array}$$

It will be seen that this agrees with the results of Ex. 54. It could be further confirmed by evaporating down the

solution obtained in these experiments and weighing the calcium chloride, when we should find that for every 100 gm. of chalk used, we get 111 gm. of dry calcium chloride.

92. Action of Hydrochloric Acid on Metals and Oxides of Metals.—The action of hydrochloric acid upon the common metals is expressed by the following equations:—

$$\begin{aligned} Zn + 2HCl &= ZnCl_2 + 2H \\ Fe + 2HCl &= FeCl_2 + 2H \\ Mg + 2HCl &= MgCl_2 + 2H \\ Al + 3HCl &= AlCl_3 + 3H \\ Na + HCl &= NaCl + H \end{aligned}$$

In all cases it will be seen that the metal takes the place of the hydrogen, combining with the chlorine to form a chloride. With oxides the action, as a rule, is similar, except that the hydrogen, instead of being set free, combines with the oxygen to form water:

$$\begin{aligned} ZnO + 2HCl &= ZnCl_2 + H_2O \\ MgO + 2HCl &= MgCl_2 + H_2O \end{aligned}$$

In the case of the peroxides, of which manganese peroxide (or dioxide) is an example, the proportion of oxygen present is more than sufficient to combine with the hydrogen equivalent to the metal, and this excess of oxygen acts upon a further quantity of hydrochloric acid, forming water and free chlorine. Thus with sodium peroxide (made by heating sodium in oxygen) we have

$$2NaO + 4HCl = 2NaCl + 2H_2O + 2Cl$$

an action which we may suppose to take place in two steps, thus:

$$\left\{\begin{aligned} 2NaO + 2HCl &= 2NaCl + H_2O + O \\ O + 2HCl &= H_2O + 2Cl \end{aligned}\right.$$

93. Test for Chlorides.—Most of the chlorides of the metals are soluble in water, but there are a few exceptions. (Have you found any?) One of these is silver chloride, which is one of the least soluble substances known. On this account a solution of silver nitrate is used as a *test* for the presence of chlorides in a solution.

Ex. 86.—Dissolve about half a gramme of silver nitrate in 2 or 3 c.c. of distilled water in a test-tube. Add drop by drop a strong solution of potassium chloride until no further precipitate is produced. Heat, shake well, filter, and evaporate the filtrate to dryness on the water-bath. Examine the precipitate of silver chloride—try whether it dissolves in nitric acid. Examine also the residue left on evaporating the filtrate. Try the action of strong sulphuric acid upon it, and convince yourself that it behaves like the potassium nitrate already used in Ex. 43.

In using this test nitric acid is always added before the silver nitrate solution. This has no action upon the silver chloride, but prevents the formatiom of other precipitates (such as silver carbonate) which might be formed were it omitted. Notice that the test is a test for *chlorides*, not for the element chlorine. Many compounds containing chlorine give no precipitate with silver nitrate. (Find out whether potassium chlorate is one of these.)

94. Double Decomposition.—The action that takes place in the last experiment is expressed by the equation:

KCl	+	$AgNO_3$	=	KNO_3	+	$AgCl$	
Potassium chloride	+	Silver nitrate	give	Potassium nitrate	+	Silver chloride	
74·5	+	170		101	+	143·5	parts by weight.

The two salts exchange metals and form two new salts in which each metal is combined with the acid that was originally combined with the other metal. The proportions by weight may be verified by weighing each of the four substances. This action is an instance of what is called *double decomposition*—a kind of chemical change that is very common and is particularly useful in qualitative analysis.

Double decomposition probably takes place to some extent in every case where solutions of two different salts are mixed. But it is only in cases where one of the two salts, like the silver chloride in the particular case we are considering, is *insoluble*, that the change is complete. If, for example, we were to mix solutions of potassium chloride and zinc nitrate we should get some zinc chloride and potassium nitrate formed. But both of these remain in solution, and a point is ultimately reached where all the four salts—potassium chloride, zinc chloride, potassium nitrate, and zinc nitrate—exist side by side without further change.

QUESTIONS AND EXAMPLES ON CHAPTER X.

1. Why cannot hydrochloric acid be collected over water? Which of the following substances could be used to dry this gas:—sulphuric acid, quicklime, calcium chloride?

2. Describe an experiment to prove that hydrochloric acid gas contains half its volume of hydrogen.

3. What is rock salt? How would you distinguish it from (*a*) nitre (see page 58), (*b*) calcite?

4. Describe with an equation how you would prepare chlorine from hydrochloric acid. What experiments would you make in order to show (*a*) its action upon metals, (*b*) its action on compounds containing hydrogen, (*c*) its bleaching action?

5. Name several substances which may be employed to set free chlorine from hydrochloric acid. What element is contained in all of these substances?

6. What weight of manganese dioxide is theoretically required to set free 14·2 gm. of chlorine from hydrochloric acid?

7. What is a chloride? What happens when strong sulphuric acid is added to a chloride?

8. What is the difference between a chloride and a chlorate? How could you show that the substance left behind when potassium chlorate is heated is a chloride?

9. Describe an experiment which shows that light is sometimes instrumental in causing chemical action. What other agent is much more frequently employed?

10. Describe two experiments to prove that quicklime contains oxygen.

11. What is the general action of hydrochloric acid (*a*) on metals, (*b*) on oxides of metals? Give equations to illustrate your answer.

12. What is meant by double decomposition? Give an example.

CHAPTER XI

SULPHUR AND ITS COMPOUNDS

95. Occurrence and Properties of Sulphur.—Sulphur is found in the form of yellow crystals in Sicily and other places in the neighbourhood of volcanoes. It has already been mentioned as an element,—one of the substances which have never so far been broken up into two different kinds of matter. We have already seen (Ex. 13) that, as ordinarily met with, it is a yellow solid, crystalline, brittle, insoluble in water but easily soluble in carbon disulphide, and crystallising from its solutions in the form of rhombic octohedrons. We have also seen that it burns in air or oxygen, and that the product of combustion is an invisible gas, which has a strong odour and dissolves in water, forming an acid liquid. Let us first make an experiment to find out the action of heat upon sulphur.

Ex. 87.—Put about 20 gm. of sulphur into a large test-tube (which must, of course, be dry). Heat it carefully, and notice the changes that take place. It will be found that the sulphur first melts (at what temperature?) to an amber-coloured or pale yellow liquid, which is quite mobile (*i.e.* flows easily, like water). At a higher temperature the liquid becomes dark brown in colour, and so thick that the tube can be inverted without anything running out. At a still higher temperature a further change occurs (describe it), and, lastly, the sulphur boils and fills the tube with a brown vapour. When this stage is reached pour the boiling liquid quickly into a basin of cold water. (The test-tube must be held by a metal or wooden holder, as the liquid is very hot, and generally takes fire on coming into contact with the air.) Examine the substance left in the basin. Describe its properties. Dry some of it, and try whether it is soluble in carbon disulphide. Weigh another portion, after drying,

and put it aside for a week. What change do you find (*a*) in its properties, (*b*) in its weight?

Ex. 88.—Melt at least 50 gm. of sulphur in a porcelain basin, supported on a piece of asbestos cardboard over a flame. When all has become liquid remove the flame, and allow the liquid to cool. As soon as a thin crust of solid has formed on the surface, pierce it in two places with a hot wire, and at once pour out the still liquid sulphur. Now remove the upper crust of solid sulphur, and examine the crystals which line the inner cavity. Compare them with those obtained in Ex. 13. Weigh a portion, and leave it to stand till next lesson. Do you find any alteration in the weight? What do you notice as to the appearance of the crystals? (Examine them with a microscope, if possible.)

From the foregoing experiments it appears that sulphur can exist in at least three different forms—as rhombic or ordinary sulphur (the native form), as plastic sulphur, and as "monoclinic" sulphur. The last is the name given to the transparent needle-shaped crystals obtained in the last experiment, and refers to the fact that the long axis of the crystals is inclined to the plane formed by the other two, instead of being at right angles to it, as in rhombic sulphur. These three forms of sulphur have different physical properties, but they are all essentially the same substance, and each can be converted into the other without alteration of weight. Moreover, all burn in air or oxygen, and form sulphur dioxide; and if equal weights of the three be taken they will form equal weights of sulphur dioxide. Many other elements can be got in different or "allotropic" [1] forms like sulphur.

96. Action of Sulphur upon Metals.—Let us next try a few experiments to show the action of sulphur on metals.

Ex. 89.—Boil a little sulphur in a test-tube, and put into the vapour a spiral of thin copper wire. Note what happens, and examine the compound produced.

Many other metals combine with sulphur like copper, forming compounds called sulphides. (Notice that names ending in "ide" are given to compounds containing only two elements. An oxide is a compound of another element with oxygen, a sulphide a compound of another element with sulphur. There

[1] From the Greek *allos*, another, and *tropos*, form.

is no rule as to which name is placed first; it is a matter of custom. Thus we might speak of water either as hydrogen oxide or oxygen hydride; but when one of the two elements is a metal, and the other a non-metal, it is usual to put the name of the metal first, and add the termination "ide" to the name of the non-metal. Thus, for example, we speak of copper oxide, zinc sulphide, calcium chloride, and so on.)

Ex. 90.—Weigh a porcelain crucible with its lid. Put into it a small piece of silver foil (0·5 to 1 gm.), and weigh again. Add 1 or 2 gm. of sulphur, cover the crucible, and heat strongly, till no smell of burning sulphur can be distinguished on removing the flame. (Five minutes will generally be long enough.) Allow to cool, and weigh. Add a little more sulphur, cover, heat again, and weigh a second time to make sure that the metal has been completely converted into sulphide. Calculate how much sulphur has combined with 108 parts by weight of silver. The silver sulphide should be preserved. The experiment may be repeated with copper instead of silver.

Ex. 91.—Weigh a crucible with its lid. Add about 1 gm. of iron in fine powder (sifted filings) and weigh again. Now add about 1 gm. of sulphur in powder and mix it well with the iron by stirring with a glass rod. Cover the crucible, heat strongly, and weigh as in the last experiment. Heat again with more sulphur as before, and take the second result if it does not differ by more than 1 cgm. from the first. If there is a greater difference the heating with sulphur and weighing should be repeated until a constant, or nearly constant,[1] result is obtained. The sulphide should be preserved for a future experiment. It will be found on comparing the results with those obtained for the equivalents of the metals that the first and third give 16 as the equivalent of sulphur (that is, the number of grammes of sulphur that can take the place of 1 gramme of hydrogen), whereas the second gives half this value. The combining weight actually chosen is a multiple of both numbers—32. The reactions with silver, copper, and iron, are therefore expressed by the equations:

$$2Ag + S = Ag_2S$$
$$2Cu + S = Cu_2S$$
$$Fe + S = FeS.$$

[1] This experiment does not give such good results as the last.

97. Action of Acids upon Sulphides. — Ex. 92.—Try the action of hydrochloric acid on the sulphides made in the last two experiments. You will find that the silver and copper sulphides are not affected, but the iron sulphide dissolves with effervescence. Note the smell of the gas that is evolved. Fit a leading tube to the test-tube and find out whether the gas is heavy or light, whether it dissolves in water, and whether it burns or supports combustion.

It is easy to show that the new gas contains sulphur, for on burning it gives the unmistakable odour of burning sulphur. If we evaporate the solution left behind in the test-tube, we shall obtain the same chloride of iron which was formed when we dissolved iron in hydrochloric acid. It therefore seems probable that the new gas is a compound of sulphur and hydrogen, since we have accounted for three out of the five elements present in the experiment. (What are they?) We can easily test this, for if the gas contains hydrogen it should form water when burned in air.

Ex. 93.—Fit up the apparatus already used in Ex. 47. Put into the bottle iron sulphide and hydrochloric acid and burn the dry gas at the jet, after making sure that all air has been expelled. Is water formed?

98. Composition of Hydrogen Sulphide.—The last experiment shows that the gas obtained from iron sulphide and hydrochloric acid is a compound of hydrogen and sulphur or hydrogen sulphide. It is more often given its old-fashioned name of "sulphuretted hydrogen." Its quantitative composition may be proved by passing it through a weighed tube containing heated copper. The copper combines with the sulphur, and the hydrogen can be measured and its weight calculated. The proportion between the weight of the two elements is found to be 16 to 1, and the formula of the gas is therefore H_2S. The formation of this gas from sulphides by the action of hydrochloric acid is exactly paralleled by that of water from oxides by the action of the same acid. Thus if we take zinc, we have the following equations:—

$$Zn + O = ZnO \qquad ZnO + 2HCl = ZnCl_2 + H_2O$$
$$Zn + S = ZnS \qquad ZnS + 2HCl = ZnCl_2 + H_2S$$

Ex. 94.—Make a solution of hydrogen sulphide by passing the gas first through a few drops of water in a test-tube and then into a bottle filled with distilled water. Test a little of the solution with litmus. What do you find? Add a few drops to a solution of silver nitrate in a test-tube. What happens? Repeat the experiment with solutions of copper sulphate and tin chloride.

99. Action of Hydrogen Sulphide on Solutions of Metallic Salts.—These experiments show that hydrogen sulphide has some of the properties of an acid. Its solution does not decompose chalk or dissolve metals with evolution of hydrogen; but it reddens litmus, and it precipitates silver sulphide from silver nitrate solution exactly as hydrochloric acid precipitates silver chloride. In both cases nitric acid is set free, as can easily be shown by filtering off the precipitate and warming the filtrate with copper foil, when we get the characteristic red fumes evolved. When metals are heated in the gas a sulphide of the metal is formed and hydrogen is set free, just as with hydrochloric acid gas, we get a chloride of the metal and hydrogen set free. These analogies are well shown by the following equations:—

$$\begin{cases} 2AgNO_3 + H_2S = Ag_2S + 2HNO_3 \\ AgNO_3 + HCl = AgCl + HNO_3 \end{cases}$$

$$\begin{cases} H_2S + Zn = ZnS + 2H \\ 2HCl + Zn = ZnCl_2 + 2H \end{cases}$$

Most of the sulphides of the metals are insoluble in water, and many have characteristic colours. Hydrogen sulphide is therefore very useful as a test for the presence of certain metals, and as a means of separating them from each other.

100. Sulphur and Oxygen.—We shall next go on to a study of what takes place when sulphur burns in air or oxygen. We have already seen that the gas which is produced dissolves in water and forms an acid solution. We should therefore expect to find that the gas combines with alkalies such as lime and caustic soda.

Ex. 95.—Put a piece of sulphur into a deflagrating spoon. Light it and allow it to burn inside a bottle of air or oxygen. Pour into the bottle a few drops of caustic soda solution, insert the stopper and shake well. Now try whether you can detect the smell of burning sulphur, or whether a piece of blue litmus paper is reddened when passed into the bottle (of

course the litmus paper must not be allowed to touch the alkaline liquid). You will find that the gas has been completely absorbed.

101. Composition of Sulphur Dioxide.—The last experiment gives us a ready means of finding out the composition by weight of the gas formed by burning sulphur in oxygen. We have only to take a weighed quantity of sulphur, burn it in oxygen, pass the gas through a weighed tube containing an alkaline solution, and find what increase is produced in the weight of the tube.

Ex. 96 (*Teacher only*).—Fit up the apparatus shown in the figure. The gas holder contains oxygen,[1] which is dried by passing

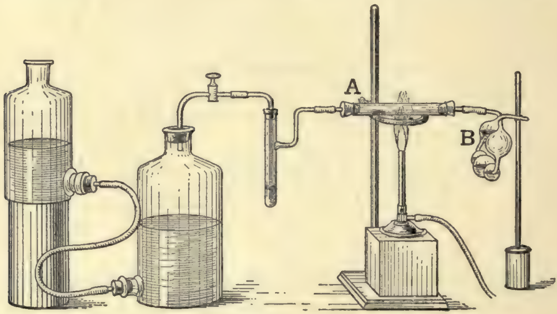


Fig. 49.

through strong sulphuric acid, and is then led into the hard glass tube which contains a weighed amount of sulphur (about ·3 gm.). The weighed "potash bulb" *B* is filled with a solution of caustic soda, or, better, caustic potash, in two to three times its own weight of water, and is supported in such a position that the bubbles of gas must pass four times through the liquid before they can escape. Some care is needed to prevent the sulphur from volatilising or "subliming" into the cold parts of the tube. The latter should be first strongly heated in the centre, and then the extreme end of the little heap of sulphur at *A* should be heated till it catches fire, when the flame should be immediately removed to the

[1] The oxygen should be made from potassium chlorate alone, or if manganese dioxide be used, the gas must be allowed to stand for a day or two to insure that it is quite free from chlorine. Air may be used instead of oxygen, but this makes the experiment more difficult.

middle of the tube again. After all the sulphur has burned away, continue to pass oxygen (about 3 bubbles per second), for ten minutes or so. Then disconnect the bulb *B*, draw air through it to replace the oxygen, allow to cool thoroughly, and weigh.

It will be found that sulphur combines with exactly its own weight of oxygen to form the gas to which we may now give its proper name of sulphur dioxide. Since the combining weight of sulphur is 32, the composition of sulphur dioxide is expressed by the formula SO_2, and its formation from sulphur by the equation:

$$\begin{array}{l} S + 2O = SO_2 \\ 32 + 2 \times 16 = \ \ 64 \end{array}$$

Sulphur dioxide, though a gas at the ordinary temperature, is easily liquefied by cold or pressure. If the gas prepared from sulphuric acid and copper be led into a test-tube cooled by a mixture of pounded ice and salt, it condenses to a colourless mobile liquid, which rapidly boils away when exposed to the air. The gas is liquefied on a large scale, and is sold in the liquid state in "syphons," from which it can be drawn off as required. One of the principal uses of the gas is for bleaching. It combines with many vegetable colouring matters to form colourless compounds, and silk, flannel, and other substances are bleached by exposure to the fumes of burning sulphur. If a little sulphur be burned under a bell-jar in which some violet or red rose petals have been placed, the colour of the flowers will gradually disappear. In most cases the colour is restored by the action of acids or alkalies. The latter action is illustrated by the familiar fact that white flannel and silk, when washed with soap, become yellow.

102. Preparation of Sulphur Dioxide.—We have already seen that sulphur dioxide is formed when metals are heated with strong sulphuric acid, and this is the method by which the gas is usually prepared in the laboratory.

Ex. 97.—Put into a test-tube or small flask 4 or 5 c.c. of strong sulphuric acid and add a few pieces of copper foil. Fit the test-tube with a cork and leading tube and collect the gas by displacement (see Fig. 45). Find out its action on a lighted taper and on burning magnesium. Pass some into a test-tube containing a little water and notice the smell of the solution and its action on litmus. Try whether it gives carbon dioxide with chalk, and hydrogen with magnesium. Allow the residue in the test-tube to cool, add a little water, heat and filter.

Pour the blue solution into a basin and allow it to stand. Blue crystals of copper sulphate will be formed.

103. Sulphurous Acid.—The liquid formed by passing sulphur dioxide into water is called sulphurous acid, and the action is supposed to be expressed by the equation:

$$SO_2 + H_2O = H_2SO_3.$$

But the acid itself is an unstable body, readily splitting up into sulphur dioxide and water, so that if boiled or left exposed to the air for a few hours, it loses its characteristic smell, and leaves behind nearly pure water. It has never been obtained in the pure state, and the formula H_2SO_3 is a conjectural one, based upon the results of analysis of the salts formed by the acid with metals. The magnesium salt, for example, consists of 24 parts by weight of magnesium combined with 32 of sulphur and 48 of oxygen. Its formula is therefore $MgSO_3$. Now we know that in other acids 24 parts by weight of magnesium always replace 2 parts by weight of hydrogen, and we therefore conclude that the acid, if it could be got pure, would be composed of 2 parts by weight of hydrogen to 32 of sulphur and 48 of oxygen, corresponding to the formula H_2SO_3.

104. Salts from Sulphurous Acid.—The salts formed by this acid are called sulphites, and their formulæ correspond to those of the carbonates. Thus magnesium carbonate is $MgCO_3$ and magnesium sulphite $MgSO_3$; calcium carbonate is $CaCO_3$, and calcium sulphite $CaSO_3$. There are resemblances in the chemical behaviour of the two classes of salts which are still more striking.

Ex. 98.—Put some calcium or sodium sulphite into a test-tube, and add strong hydrochloric acid or sulphuric acid. Notice that a gas is given off. What is it? Evaporate the solution. What do you obtain?

The reaction that takes place in this experiment, using calcium sulphite and hydrochloric acid, may be written

$$CaSO_3 + 2HCl = CaCl_2 + H_2O + SO_2$$

corresponding exactly to

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

This experiment is sufficient to show that the sulphites and carbonates are closely related.

105. Tests for Sulphites.—The evolution of sulphur dioxide by the action of hydrochloric, or, better, strong sulphuric acid, is the best test for sulphites. The gas is recognised by its smell and by its bleaching action. (An infusion of rose leaves is at once bleached by it.) Another test for sulphites is a solution of barium[1] chloride. This gives a white precipitate of barium sulphite when added to a solution of a sulphite. The reaction is a double decomposition—*e.g.*

$$MgSO_3 + BaCl_2 = MgCl_2 + BaSO_3$$

The white precipitate is instantly dissolved by hydrochloric acid, being converted into barium chloride, while at the same time sulphurous acid is set free, which may or may not split up (according to the amount of water present) into sulphur dioxide and water.

Ex. 99.—Take some freshly-made strong sulphurous acid in a test-tube, and add to it caustic soda solution little by little, until after shaking the solution it no longer smells of sulphur dioxide. Now add barium chloride solution. Notice the dense white precipitate of barium sulphite. Add hydrochloric acid. What happens?

106. Action of Oxidising Agents upon Sulphurous Acid.—Ex. 100.—Take about 10 c.c. of strong sulphurous acid in a boiling tube. Add 2 or 3 c.c. of strong nitric acid. Heat, and notice what happens. Now boil down the liquid until only 2 or 3 c.c. are left. Cool and examine this residue, which should not smell of nitric acid. Notice its oily consistency. Add water and notice that heat is evolved. Add a drop of the diluted liquid to some barium chloride in another test-tube. Is the precipitate which you obtain dissolved by hydrochloric acid? Dip a glass rod into the remainder of the liquid. Trace some letters with it on paper, and notice what happens when the paper is warmed over a gas flame till the letters are dry.

These experiments show that by heating sulphurous acid with nitric acid, it is converted into sulphuric acid.[2] The usual action of nitric acid upon other substances is to introduce oxygen into them, and it is not difficult to show that this

[1] Barium is a comparatively rare metal, which is very closely related in its properties and those of its compounds to calcium.

[2] The formation on adding barium chloride of a white precipitate which is *insoluble* in hydrochloric acid is a characteristic test for sulphuric acid and sulphates. The charring of paper on drying, after being wetted with the acid, is a good test for free sulphuric acid itself.

is what takes place here, for the same change can be brought about, though much more slowly, by the action of oxygen itself upon sulphurous acid.

Ex. 101.—Take a bottle of at least 300 c.c. capacity, with a tight-fitting stopper which should be slightly greased. Put into it 4 or 5 c.c. of dilute sulphurous acid and fill the rest of the bottle with oxygen by displacement. Insert the stopper tightly and leave it for a week, at the end of that time examine the liquid. It will probably no longer smell of sulphur dioxide, but in any case it will give the characteristic tests for sulphuric acid after it has been boiled down to a small bulk. The last experiment proves conclusively that sulphuric acid is sulphurous acid plus oxygen. In like manner sulphates differ from sulphites by containing a larger proportion of oxygen, and in fact most sulphites absorb oxygen and gradually change into sulphates, when exposed to the air. Nitric acid, chlorine water, and other oxidising agents bring about the same change more rapidly.

107. Quantitative Composition of Sulphates.—The following experiment brings out the ratio between the weights of sulphur, magnesium, and oxygen in magnesium sulphate, the substance formed in Ex. 70, and hence by inference gives us the composition of sulphuric acid.

Ex. 102.[1]—Weigh out into a dry test-tube about 0·3 gm. of powdered sulphur (roll sulphur, or better, crystals obtained from a solution in carbon disulphide). Add 10 c.c. of pure *fuming* nitric acid, put the test-tube into a beaker of water, and heat the water to about 70° by a small flame, until all the sulphur has disappeared. This may require two or three hours. Now pour the liquid into a weighed porcelain basin, washing out the test-tube three or four times with a few drops of water from the wash-bottle, and evaporate it on a water-bath in the fume chamber until it no longer smells of nitric acid. (By this process the sulphur is completely converted into sulphuric acid. Unfortunately this cannot be weighed as such, because of the difficulty of getting it free from water.) Now weigh out accurately about 0·4 gm. of clean magnesium ribbon. Dilute the sulphuric acid in the basin, with about 5 or 6 c.c. of distilled water, and add the

[1] This experiment is too tedious to be done individually by each member of the class. It should be done by the teacher, the members of the class assisting and noting all results.

magnesium gradually in small pieces, keeping the basin covered with a watch-glass to avoid loss during the effervescence. Heat on the water-bath till no more hydrogen is evolved, and then remove any undissolved magnesium with a pair of forceps, washing any solution that adheres to it back into the basin with a little distilled water from the wash-bottle. Finally evaporate to dryness on the water-bath, and heat the basin by a small flame (using a "rose" on the Bunsen burner, and keeping the basin two or three inches above it) until its weight is constant. Weigh also the undissolved magnesium, and find out how much has combined with the acid. Calculate how much magnesium would combine with the sulphuric acid formed from 32 gm. of sulphur, and how much magnesium sulphate would be formed. (In an actual experiment ·296 gm. of sulphur was taken; the weight of magnesium used was ·217 gm., and that of the magnesium sulphate was 1·110 gm. These numbers are in the proportion 32 : 23·5 : 120. The formula $MgSO_4$ requires 32 : 24 : 120.)

This experiment shows that magnesium sulphate has the composition $MgSO_4$, and if we replace the magnesium by the equivalent weight of hydrogen, as found in Exs. 69 and 70, sulphuric acid must have the formula H_2SO_4. Its formation from sulphurous acid may therefore be expressed by the equation:

$$H_2SO_3 + O = H_2SO_4.$$

108. Properties of Sulphuric Acid.—It is clear from what has gone before that to the chemist sulphuric acid is a very important substance. It is used in the preparation of most other acids (hydrochloric and nitric for example), as a drying agent, and for many other purposes. From the experiments in Chap. VII. you already know that it acts upon metals in two different ways, according as the dilute or concentrated acid is used. In the first case hydrogen and a sulphate of the metal are formed—that is, if there is any action at all. In the second case no hydrogen is evolved, but sulphur dioxide, water, and a sulphate of the metal are formed:—

$$Zn + H_2SO_4 = ZnSO_4 + 2H$$
$$Zn + 2H_2SO_4 = ZnSO_4 + 2H_2O + SO_2$$

The second reaction may be supposed to be caused by the action of the hydrogen at the moment of its liberation upon the oxygen of the sulphuric acid—thus:

$$2H + H_2SO_4 = 2H_2O + SO_2.$$

With copper the main[1] action is

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

109. Names of Salts formed from Sulphuric and Sulphurous Acids.—The salts produced by replacing the hydrogen of sulphuric acid by metals are called sulphates. Notice that the salts of sulphurous acid are called sulphites — those of sulphuric acid sulphates. It is a general rule that when an element forms two different acids by its union with oxygen and hydrogen, a name ending in "ous" is given to the acid containing the smaller proportion of oxygen, and one ending in "ic" to that which contains the larger proportion. Thus we have sulphurous and sulphuric, nitrous and nitric, phosphorous and phosphoric acids. From these the names of the salts are derived, sulphurous acid giving sulphites, nitrous acid nitrites, phosphorous acid phosphites; while sulphuric acid gives sulphates, nitric acid nitrates, and phosphoric acid phosphates.

110. Sulphates.—Most of the sulphates, as we have already seen, can be prepared by the action of sulphuric acid on the metals. They may also be got by acting upon the oxides with sulphuric acid. Here, as in the case of hydrochloric acid, the only difference in the result is that water is formed instead of hydrogen when the oxide is used instead of the metal. Thus, for example, zinc oxide and sulphuric acid give zinc sulphate and water. Most of the sulphates are easily soluble in water, but those of calcium, barium, and lead are exceptions. Consequently when sulphuric acid is added to a solution containing one of these metals, a precipitate of the sulphate is produced. The action is a double decomposition.

$$BaCl_2 + ZnSO_4 = BaSO_4 + ZnCl_2.$$

111. Water of Crystallisation.

EX. 103.—Heat some crystals of copper sulphate (those obtained in Ex. 97 may be used) in a dry test-tube, held horizontally, and note what happens. What is the liquid that condenses in the cold

[1] In the case of both copper and zinc the action is really more complicated than is shown by these equations. Small quantities of copper sulphide are formed in the first case, while hydrogen sulphide and sulphur are set free in the second.

part of the tube? Take out some of the white powder that remains, place it on a watch-glass, and add a drop of water. What happens?

Many other salts beside copper sulphate combine with water in crystallising, and give up this water again on heating. This combined water is called "water of crystallisation." It is quite definite in amount, but the proportions contained in different salts are very different. When it is driven off by heat, the crystals fall to powder. In some cases this water is gradually given off when the crystals are merely exposed to the air at the ordinary temperature. Such substances are said to "effloresce" on exposure to air.

Ex. 104.—Find which of the following substances contain water of crystallisation. Alum, ferrous sulphate, potassium sulphate, sodium sulphite, potassium nitrate, zinc sulphate.

In general, the proportion of water of crystallisation may be determined quantitatively by heating the *powdered*[1] crystals in a crucible which may be heated directly by a small flame three or four inches below it. A better plan is to use a sand-bath—a thin iron basin filled with dry sand in which the crucible is partly embedded. This gives a steady and moderate heat and avoids the danger of decomposing the salt itself by too high a temperature. The heating must be continued *till the weight is constant.*

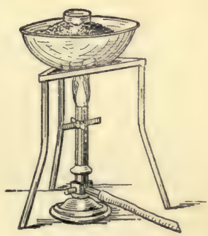


Fig. 50.

Ex. 105.—Determine the proportion of water of crystallisation in any of the following—magnesium sulphate, copper sulphate, barium chloride. Use one to two grammes in each case.

112. Sulphur Trioxide.—Another compound of oxygen and sulphur is known in addition to sulphur dioxide. When a mixture of sulphur dioxide and oxygen is passed over warm finely-divided platinum and the product is led into a cold receiver, we get white silky-looking crystals which contain 32 parts by weight of sulphur

[1] When crystals are heated without being previously powdered there is danger of loss, owing to small explosions caused by the sudden conversion of mechanically retained water into steam.

to 48 of oxygen, and have therefore the formula SO_3. This substance is called sulphur trioxide. It dissolves instantly in water with a hissing noise and great evolution of heat, and the result of the combination is sulphuric acid. It follows that sulphur trioxide stands in the same relation to sulphuric acid as sulphur dioxide to sulphurous acid. It is the *acid-forming oxide* or *anhydride* (see p. 87) of sulphuric acid. It is often called sulphuric anhydride, and in the same way sulphur dioxide is called sulphurous anhydride, the names implying, of course, that these bodies combine with water, forming respectively sulphuric and sulphurous acid according to the following equations:—

$$SO_3 + H_2O = H_2SO_4$$
$$SO_2 + H_2O = H_2SO_3$$

QUESTIONS AND EXAMPLES ON CHAPTER XI.

1. What gaseous compounds of sulphur do you know, and how would you prepare each of them from ordinary "flowers of sulphur"?

2. How can it be proved that ordinary sulphur and plastic sulphur, though differing very much in properties, have the same chemical composition? Do you know any similar case of a *compound* existing in different forms? (See page 75.)

3. What is a sulphide? What is the meaning of the termination "ide" in chemical names?

4. How would you show by experiment that hydrogen sulphide has some of the properties of an acid? What name is given to the salts derived from it?

5. How could you prove that hydrogen sulphide contains (*a*) hydrogen, (*b*) sulphur? Sketch the apparatus you would use in each case.

6. What is the equivalent of sulphur (*a*) to hydrogen, (*b*) to oxygen? If the combining weight of sulphur were taken as 16 instead of 32, what would be the formula of sulphuretted hydrogen?

7. What is a sulphite? How could you prepare sulphur dioxide from a sulphite? Give an equation.

8. How can sulphites be converted into sulphates? Give an equation to illustrate your answer.

9. What is the usual action of nitric acid upon other substances? Give two examples. (See page 96.)

10. How could you distinguish a sulphite from (*a*) a sulphate, (*b*) a carbonate?

11. Point out the resemblances and differences between sulphurous acid and carbonic acid.

12. What is meant by water of crystallisation? How can its amount be determined? Name two salts which, as usually met with, contain water of crystallisation, and two which do not.

13. What is an anhydride? Give three examples.

14. What volume of sulphur dioxide (relative density = 32) could theoretically be got by the action of 6·3 gm. of copper on strong sulphuric acid?

15. What weight of iron sulphide would be needed to give 170 gm. of hydrogen sulphide by the action of an acid?

CHAPTER XII

CARBON AND ITS COMPOUNDS

113. Action of Heat upon Wood and Coal.—We have seen in Chap. VIII. that the element carbon occurs in chalk in combination with calcium and oxygen, and also in wood, wax, oil, and spirit of wine combined with hydrogen.

Ex. 106.—Put a few pieces of hard wood into a dry test-tube furnished with a cork and leading-tube. Support the test-tube horizontally as in Fig. 14 and heat it. You will find that a gas is evolved and that a liquid collects in the cold part of the tube. Collect the gas over water, and when no more is evolved remove the apparatus and allow it to cool. Examine the gas. Is it combustible? Does it contain carbon? Test the liquid with litmus paper. Take out the black residue and examine it. Describe its properties and find out what happens when it is heated in an open crucible. In this experiment we have imitated, on a small scale, the process used when making charcoal from wood. The process is called "destructive distillation." It differs from ordinary distillation in the fact that the volatile substances which condense in the cold part of the apparatus were not originally present in the substance distilled but were produced by its breaking up, or destruction—hence the name.

Ex. 107.—Repeat the last experiment, using a hard glass tube filled with coal. What differences and resemblances do you notice?

This is the method by which coal-gas is made, and the black substance left behind in this case is called coke. Charcoal and coke are nearly pure carbon—not quite pure, for they always contain a little hydrogen and they always leave behind a little ash when burned. The hydrogen can be removed by heating in chlorine, with which it combines to form hydrochloric acid; and most of the mineral matter can be removed by treatment with acids. A still purer form of carbon can be

got from soot or lampblack, which is formed by burning oil, wax, etc., with an insufficient supply of air. This substance when heated in chlorine leaves pure carbon behind as a dull black powder. All these forms of carbon, though differing considerably in their physical properties, are alike in this, that all burn in oxygen, forming forty-four parts by weight of carbon dioxide for every twelve parts by weight of carbon that are taken.

114. Other forms of Carbon. — All the forms of carbon hitherto mentioned are artificial products and are amorphous —without crystalline form. But in addition two other forms of carbon are found naturally, and both of these are crystalline. One is diamond, which is found in transparent octahedral crystals in South Africa, Brazil, and India. The other is graphite or black-lead, which occurs in Cumberland and at various places in Siberia and other countries, and has an entirely different crystalline form from diamond. Beside its transparency and its beauty as a gem, diamond is remarkable as being the hardest of all known substances. No other substance can be made to scratch it. Hence the phrase, "diamond cut diamond." When strongly heated in air or oxygen both diamond and graphite burn and form carbon dioxide, just as do charcoal and coke. If equal weights of diamond, graphite, and pure charcoal be burned in oxygen, they form equal weights of carbon dioxide and nothing else. Hence, these three substances, though so very different in appearance, are all allotropic forms of the same element, carbon. It is not difficult to show that diamond burns in oxygen and forms carbon dioxide.

EX. 108 (*Teacher only*).—Procure a small splinter of diamond. Sufficient may be bought for a shilling or two. Take a piece of glass tubing about 30 cm. long and drawn out to a jet at one end. Put the end of a piece of thin platinum wire about 6 cm. long into the jet, so that 4 or 5 mm. of the wire is inside the glass. Hold the point of the jet in the Bunsen flame, and turn it round constantly till the opening has closed round the platinum, which is now held firmly by the glass. Wrap the free end of the wire repeatedly round the splinter of diamond, so as to make a tiny cage for it, from which it cannot drop out. Fill a glass bottle or jar with oxygen (free from

carbon dioxide[1]) and pour a little clear lime-water into the bottle. Now heat the diamond strongly in the blow-pipe flame, and when red hot, plunge it quickly into the oxygen. It will glow brightly for some time, and on shaking up the lime-water the characteristic precipitate of chalk will be formed. The experiment may be repeated with graphite.

The last experiment has been carried out with weighed quantities of diamond and graphite, with the result already stated, that for every 12 parts by weight of either substance, 44 parts by weight of carbon dioxide are produced. The apparatus used was in all but details the same that we employed in Ex. 96, to find the proportions in which sulphur and oxygen combine. The cost of diamond, unfortunately, makes the experiment impracticable for us. But it should be carried out with pure charcoal, and the results compared with those given here.

115. Carbon and Oxygen.—The method of preparing carbon dioxide, its properties and its composition, have already been dealt with in Chap. VIII. We have found that it is a colourless invisible gas, which neither burns nor supports combustion, and is about one and a-half times heavier than air, so that it can be collected by downward displacement, and poured downwards from one vessel to another. In the laboratory it is usually prepared by the action of an acid upon chalk or marble. But it is also formed by burning carbon (and many substances which contain carbon) in air or oxygen, and in many other ways. Like all other gases, it can be liquefied by cold and pressure, and large quantities of the liquid are now sold for aërating beverages. When the liquid is allowed to evaporate rapidly so much heat is absorbed in the evaporation of a portion of it that the remainder is cooled below its freezing point and appears as a white snow-like solid.[2] Since carbon dioxide contains carbon and oxygen in the proportion of three parts by weight of carbon to eight of oxygen, its formula is CO_2. The relation between its volume and that of the oxygen it contains may be shown by the following experiment:—

[1] The oxygen must be made from potassium chlorate alone, for commercial manganese dioxide always contains a little carbon, which burns when it is heated with potassium chlorate, forming carbon dioxide.

[2] For an easy way of making small quantities of solid carbon dioxide from the "sparklets" now sold everywhere, see note by Professor Wood in *Nature* for May 1st, 1902.

Ex. 109 (*Teacher only*).—Fit up the apparatus shown in the figure. The round-bottomed flask is filled by displacement with oxygen. The conical spiral of aluminium wire, *A*, slides on the glass tube *T*. In *A* is placed a small piece of charcoal (which should have been previously heated in chlorine to ensure that it is free from hydrogen). The charcoal is ignited by passing an electric current (from three or four Bunsen cells) through the insulated copper wires *A*, *A* which pass through the tube *T*, and are connected at the bottom by a short piece of thin platinum wire, which becomes red-hot when the current passes. (The wires pass out through two small holes—made with a wetted file—at the lower end of *T*, and after their insertion the tube is filled up with plaster of Paris made into a thin cream with water). In the bottom of the flask is a little dry sand. The U tube, which passes air-tight through the india-rubber stopper *S*, contains mercury, which by its movement serves to show any alteration in the volume of the gas inside the flask. When all is ready, the stopper is inserted tightly, and the wires *A*, *A* are connected to the battery. During the combustion of the charcoal the mercury shows a considerable expansion, but this is due entirely to the heat evolved by the combination of the carbon and oxygen; and when the action is over, and the apparatus has cooled down, the mercury returns to its original position, showing that *the carbon dioxide produced occupies exactly the same space as the oxygen from which it was formed.*[1]

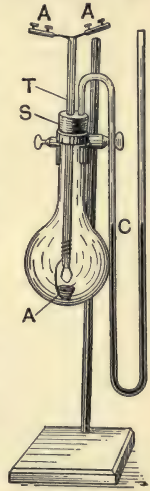


Fig. 51.

116. Sodium Carbonate.—We have seen that carbon dioxide, like sulphur dioxide, has acid properties. Its solution in water changes the colour of blue litmus to a purplish red, and it combines readily with lime, forming chalk or calcium carbonate.

[1] A simpler method of performing this experiment is to use a hard glass tube like that shown in Fig. 21 (but not graduated). The tube is filled with dry oxygen, a piece of charcoal is introduced, and the stopper is inserted very tightly. The clip is opened for a moment to equalise the pressure and then closed. The charcoal is ignited by holding the closed end of the tube in the Bunsen flame, and after it has burned and the apparatus has become cold, the mouth of the tube is placed under mercury and the clip is opened. No mercury enters and no gas escapes, showing that the volume of gas has not altered.

Many other carbonates are known. The most important is sodium carbonate or soda-ash.

Ex. 110.—Determine the proportion of carbon dioxide in soda-ash (anhydrous sodium carbonate) by the method used in Ex. 54. Calculate the weight of carbonate that contains 44 parts by weight of carbon dioxide.

Ex. 111. — Weigh out about 1 gm. of soda-ash. Add hydrochloric acid till no further effervescence takes place. Evaporate to dryness, and weigh the sodium chloride which is left. Knowing that common salt has the formula NaCl calculate what weight of sodium was contained in the soda-ash. Afterwards calculate what weight of sodium carbonate contains 23 parts by weight of sodium.

It will be found that the composition of sodium carbonate is expressed by the formula Na_2CO_3—*i.e.* that 46 parts by weight of sodium and 44 of carbon dioxide are contained in 106 parts by weight of the carbonate. The equation for the reaction with hydrochloric acid is therefore

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O.$$

117. Carbonic Acid.—It will be seen that both calcium and sodium carbonates may be regarded as derived from a hypothetical carbonic acid, H_2CO_3, by replacing hydrogen by the equivalent quantity of calcium or sodium. This hypothetical acid is supposed to exist in the solution formed by passing carbon dioxide into water, but, like sulphurous acid, it has never been got in the pure state. If we try to separate it, we always get, not carbonic acid, but carbon dioxide and water.

118. Other Carbonates. — Most of the other carbonates are insoluble in water and are got from sodium carbonate by double decomposition (see p. 117).

Ex. 112.—Add sodium carbonate solution to a solution of barium chloride or zinc sulphate in a test-tube until no further precipitate is produced. Filter off the precipitate, wash it till free from sodium carbonate (test the washings with litmus paper), and then find out its behaviour (*a*) when heated on a loop of thin iron wire, (*b*) when treated with hydrochloric acid before and after heating.

Most of the carbonates are decomposed by heat, like calcium

carbonate, leaving the oxide of the metal. A few are unaltered. All are decomposed by acids (hydrochloric acid, nitric acid, sulphuric acid, sulphurous acid), with evolution of carbon dioxide.

119. The second Oxide of Carbon.—Besides carbon dioxide, another compound of carbon and oxygen is known. This substance is likewise a gas, and it is formed by the action of red-hot iron upon carbon dioxide.

Ex. 113.—Fit up the apparatus shown in Fig. 52. Fill the hard glass tube (which should be of rather narrow bore—say, 1 cm.) with coarse iron filings, or borings. Heat it as strongly as possible and pass a *slow* stream of carbon dioxide over it. Collect the gas over water. Test it with a light. What do you find?

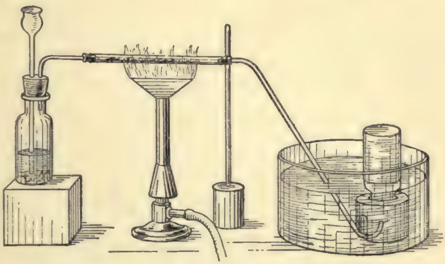


Fig. 52.

Ex. 114.—Fill a long narrow test-tube with the gas. Close it with the thumb and remove it from the pneumatic trough. Pour in quickly a few c.c. of strong caustic soda solution. Close the tube tightly with the thumb, shake violently for a minute or two, and then open it under water. What happens? Lift the tube above the water so that the caustic soda solution runs out, close it with the thumb again, insert the jet of the wash-bottle between the thumb and the rim of the tube and force in a little distilled water. Shake well, close the tube, invert it, and let the water run out. Repeat this process twice, so as to wash away all the sodium carbonate solution formed by the action of the caustic soda on the unchanged carbon dioxide present in the gas. Finally pour in a little clear lime-water and shake up. No turbidity is produced. Now put a light to the gas—it burns rapidly, and on shaking up again the lime-water becomes milky.[1]

[1] This experiment will fail unless the iron has been hot and the

This experiment shows (1) that the new gas does not combine with caustic soda (*i.e.* has no acid properties), (2) that it does not act on lime-water, (3) that in burning it combines with oxygen and forms carbon dioxide. Since it is formed by the action of iron upon carbon dioxide, and since it combines with oxygen to form carbon dioxide, it must be an oxide of carbon, but containing a smaller proportion of oxygen than carbon dioxide.

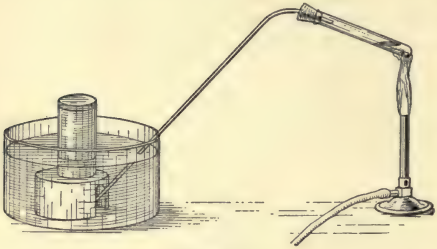


Fig. 53.

This gas, which is known as carbon monoxide, or carbonic oxide, is readily obtained pure from formic acid or its salts by heating them with strong sulphuric acid.

Ex. 115.—Heat a few grammes of sodium formate with strong sulphuric acid in a test-tube and collect over water the gas which is given off. Find out

1. Whether it is heavier or lighter than air,
2. Whether it is soluble in water,
3. Whether it has any action on lime-water,
4. The proportion of air with which it must be mixed in order to give the most rapid combustion.

120. Formula of Carbon Monoxide.—Accurate experiments show that the density of carbon monoxide is 14. 1 litre of it at N.T.P. therefore weighs $\cdot 09 \times 14 = 1 \cdot 26$ gms. Its composition may be determined indirectly by finding the volume of carbon dioxide produced from a given volume of the monoxide. This experiment may be done by burning it with oxygen in the eudiometer.

Ex. 116 (*Teacher only*).—Pass about 10 c.c. of carbon monoxide (made in a test-tube from sulphuric acid and sodium formate) into

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stream of carbon dioxide slow, so that the gas does not contain much unaltered carbon dioxide. The tube containing the iron may with advantage be covered by a strip of asbestos paper bent into a semi-cylindrical form.

the eudiometer. (See Ex. 48 for full directions how to do this.) Adjust the level and read off the volume of the gas. Now pass in about an equal bulk of oxygen, adjust the mercury, and read off the volume. Close the open limb of the eudiometer, and pass the spark. Adjust the level of the mercury again, and read off the volume. It will be found that some of the gas has disappeared, and that this contraction equals half the volume of carbon monoxide originally taken. Now run out most of the mercury by the tap, and then tilt the apparatus, and by means of a pipette, force a little caustic soda solution into the closed limb, taking care not to introduce any air along with it. Shake gently for a little, adjust the level once more (compensate for the caustic soda solution in the closed limb by putting an equal height in the open one), and read off the contraction caused by the absorption of the carbon dioxide. It will be found to be equal to the volume of the carbon monoxide used.

This experiment shows that 1 litre of the new gas combines with $\frac{1}{2}$ litre of oxygen to form 1 litre of carbon dioxide. Substituting the weights at N.T.P. for these volumes, we have 1·26 gm. of carbon monoxide combines with ·72 gm. of oxygen, forming 1·98 gm. of carbon dioxide. But we know that this weight of carbon dioxide is made up of 1·44 gm. of oxygen and ·54 gm. of carbon. Hence 1 litre of carbon monoxide contains ·54 gm. of carbon and ·72 gm. of oxygen, or in the proportion of 12 of carbon to 16 of oxygen. The formula is therefore CO.

121. The Law of Multiple Proportions.—The composition of the two oxides of carbon furnishes a very striking example of a general law, which is found to hold good whenever two elements unite in two different proportions to form different compounds. It is found that *the different weights of the second element, which combine with a fixed weight of the first, have always a simple relation to each other.* In this case, for example, we have in carbon monoxide 12 parts by weight of carbon to 16 parts by weight of oxygen; while in carbon dioxide we have 32 parts by weight of oxygen combined with the same amount of carbon. The ratio between the different weights of oxygen that combine with a fixed weight of carbon is therefore 16 to 32, or $\frac{1}{2}$. The statement of this regularity in the composition of pairs of compounds containing the same two elements is generally known as the law of multiple pro-

portions. Other examples have already been mentioned—*e.g.* sulphur dioxide and sulphur trioxide (what is the ratio between the weights of oxygen to a fixed weight of sulphur in this case?).

122. Other Methods of preparing Carbon Monoxide.—Carbon monoxide is probably formed in small quantity whenever carbon is burned in an insufficient supply of oxygen. The blue flames that are seen playing over the surface of a glowing fire of coke or cinders are due to this gas, which is formed within the fire by the action of the red-hot carbon upon the carbon dioxide, produced by the combustion of the carbon at the bottom where the air supply enters.

$$C + 2O = CO_2$$
$$CO_2 + C = 2CO.$$

The gas may be prepared by this reaction in the laboratory, but the temperature required is so high that a metal tube and a gas furnace must be used.

Carbon monoxide is a very poisonous gas—even a very minute proportion in the atmosphere of a room is sufficient to cause headache, while less than 1 per cent causes death in a short time. The poisonous action of coal-gas is due to the presence of carbon monoxide, and the fact that this gas is given off from charcoal fires has often led to fatal accidents, through the burning of charcoal in stoves without proper ventilation.

Ex. 117.—Pass carbon monoxide over copper oxide in a hard glass tube. What happens? What becomes of the carbon monoxide? How can you prove that it is changed?

Many other oxides when heated in carbon monoxide are reduced to metal, the carbon monoxide being at the same time oxidised to carbon dioxide. Carbon monoxide then, like hydrogen, is a reducing agent.

123. Compounds of Carbon and Hydrogen.—The number of compounds of these two elements is very great—some hundreds are known—but we shall notice only a few of these.

Marsh Gas or **Methane** is one of the gases present in ordinary coal-gas, and is also given off by decaying vegetable matter at the bottom of ponds and marshes (hence the name).

Its formula is CH_4. It burns with a flame that is only slightly luminous.

Acetylene.—This gas is now made on the large scale by the action of water on a compound called calcium carbide, which is made by heating quicklime to an extremely high temperature with carbon.

Ex. 118.—Throw a small piece of calcium carbide into water, and collect the gas that is evolved in a jar. Transfer portions of it to test-tubes, and find out whether it is light or heavy, whether it is soluble in water, and what proportion of air must be mixed with it in order to produce the most powerful explosion.

What becomes of the calcium contained in the carbide?

124. Combustion.—By combustion or burning, we mean the chemical combination of two substances (at least one of which is usually a gas) with evolution of heat and light. In ordinary cases the gas is oxygen, and consequently we are accustomed to speak of bodies that contain carbon or hydrogen in large proportion as combustible bodies, since these elements readily unite with oxygen, and evolve much heat in doing so. On the other hand, gases such as oxygen, which allow these substances to burn in them, are called supporters of combustion. It must not be forgotten that the action depends as much on the one substance as on the other, and, when both are gases, it is purely a matter of custom that decides which is to be called the combustible and which the supporter of combustion. It is just as easy to burn a jet of chlorine in an atmosphere of hydrogen as it is to burn a jet of hydrogen in an atmosphere of chlorine, and the chemical action is exactly the same in both cases. In like manner we may burn a jet of air or oxygen in an atmosphere of coal-gas.

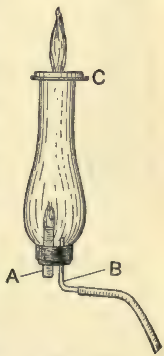

Fig. 54.

Ex. 119.—Take an ordinary lamp-glass and fit it up as shown in the figure. *A* is a tube about 4 cm. long and 1 to $1\frac{1}{2}$ cm. bore. *B* is narrower. *C* is a metal plate (the lid of a tin can will do) in which a hole about 5 mm. in diameter has been drilled. Attach *B* to the gas tap, turn on a moderate supply of gas

and light it at *C*. Now apply a light at *A*, and gradually reduce the supply from the tap until the flame passes up the tube *A* and burns inside the lamp-glass. We have thus a flame of coal-gas burning in air at *C*, and one of air burning in coal-gas inside the glass.

125. Flame.—As a rule, an ordinary flame consists of three parts,—an inner cone of unburnt gas, an intermediate one in which gas and air are meeting and combining, which may be called the zone of partial combustion, and an outer cone or mantle of very hot but almost invisible gases, the products of combustion.

Ex. 120.—Cut off a small piece of wax from a candle. Put it into a narrow dry test-tube and heat it strongly. Note what happens, and try to light the vapour which issues from the mouth of the tube. What do you find?

Ex. 121.—Blow out a candle and then at once hold a lighted match about an inch above the wick. You will find that the stream of gas rising from the wick will take fire. If the candle be surrounded by a short wide glass chimney, or a piece of paper bent into cylindrical form so as to protect it from draughts, it may be relighted from a height of 3 or 4 inches above the wick.

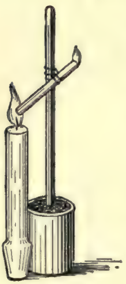

Fig. 55.

Ex. 122.—Hold a piece of glass tubing about 8 cm. long, and of 0·6 cm. bore obliquely with one of its ends in the centre of a candle flame. Note the whitish vapour which issues from the mouth of the tube: put a light to it and it will burn.

Ex. 123.—Hold a piece of thin cardboard horizontally across the centre of a candle flame. Remove it as soon as it begins to char. You will find that the charred portion has the form of a ring, showing that the centre of the flame is comparatively cold. Note also the deposition of soot on the under side of the cardboard.

Ex. 124.—Cut out a piece of cardboard the size and shape of an ordinary gas flame. Hold it between the eye and the flame, and then shake a duster or strike a match close to it. Notice the outer mantle surrounding the flame, which now becomes visible.

These experiments bring out some of the chief phenomena of flames. The centre of the flame, as has been said, consists of unburnt gas. In the case of the flame of a candle, this gas is formed by the destructive distillation of the wax, which is drawn up into the wick by capillary attraction and is then heated to the point at which it breaks up into a mixture of gases. In the intermediate zone (*b* in Fig. 56) the supply of oxygen is insufficient for complete combustion, and there are innumerable particles of white-hot solid carbon. It is from these particles that almost all the light given out by the flame is derived. In the outer flame (*c* in Fig. 56) the combustion is complete, the particles of carbon have been converted into carbon dioxide and the hydrogen of the wax into water. This part of the flame contains no solid particles, and is therefore almost invisible. When the duster is shaken near it, the particles of dust which enter it are heated till they become white-hot or incandescent, and the light they give out renders the flame visible. In the ordinary Bunsen burner air is drawn in through the holes at the bottom of the burner and mixes with the gas as it ascends the tube. When this air is in the proper proportion, a blue flame is produced which contains no carbon particles and therefore does not deposit soot and gives out very little light. That it is very hot is shown in the Welsbach burner, which is merely an ordinary Bunsen burner, in the flame of which is hung a "mantle," composed of infusible material which is heated to whiteness by the flame and gives out a very brilliant light.

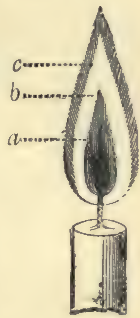

Fig. 56.

126. The Blowpipe.—A still hotter flame can be got when air under pressure is forced into the flame. This is done by the blowpipe, which is used by jewellers in soldering and by chemists in reducing metals from their compounds.

Ex. 125.—Take a piece of well-burnt charcoal, and with the point of your knife scrape out a *shallow* hole in it large enough to hold one half of a pea. Put into it *a very little* lead oxide. Now close the holes at the bottom of a Bunsen burner (or drop a special jet into the tube) so as to get a

yellow smoky flame which should be about two inches high. Rest the point of the blowpipe on the burner just inside the flame and blow gently, directing the flame on to the lead oxide.

Fig. 57.

In a short time [1] you will obtain a glistening bead of metallic lead, which may be allowed to cool and then removed, when it can be identified by the fact that it is easily flattened when pressed with a knife-blade on a hard surface, such as a penny, and leaves a grey mark when drawn over paper.

The reduction of the lead oxide to metal is brought about by the combination of the oxygen which it contains with the carbon of the coal-gas and the charcoal support. Many other metals can be reduced from their oxides in this manner. When a jet of oxygen is used in the blowpipe instead of air, we get a very small, but extremely hot flame, in which even platinum melts quite readily.

127. Ignition Point.—The continuance of any combustion depends upon whether the heat given out is sufficient to continually raise a fresh portion of the combustible material to the temperature at which it is able to combine with oxygen. If from any reason the heat evolved is not sufficient for this, the combination will cease and the flame will "go out." When a candle is burned in a closed bottle, this result is brought about by the dilution of the air with carbon dioxide, which cools the flame in two ways—first, by preventing it from receiving a sufficient supply of oxygen, and second, by using up much heat in expanding the waste gases. The flame does not go out because there is no oxygen left. As a matter of

[1] Some practice is required to keep up the jet of air sufficiently long. The student should learn to keep the cheeks distended, and at the same time draw air periodically into the lungs through the nose. This should be practised first with the mouth closed, and then with a blowpipe having a very fine jet.

fact, only about one-seventh of the oxygen has been converted into carbon dioxide when the combustion becomes so feeble that the flame can no longer keep up the supply of gas heated to ignition point. In the case of phosphorus, practically all the oxygen is used up, the reasons being (1) that the ignition point of phosphorus is *very low*—under 100° C. (whereas that of the "candle gas" is very high), (2) that the product of combustion is not a gas, but a solid, and therefore does not interfere with the action.

Ex. 126.—Roll a piece of stout copper wire tightly round a pencil so as to make a close coil about 1 cm. long. Lower this carefully into the flame of a candle so that the coil surrounds the wick (Fig. 58). The flame will be extinguished. Now relight the candle, heat the coil red-hot in the Bunsen flame, and repeat the experiment. What do you find? In this experiment, the flame is cooled below the ignition point by the conduction of so much heat into the cold metal.

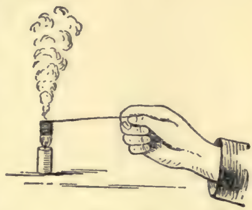

Fig. 58.

Ex. 127.—Close the air holes at the base of your Bunsen burner. Light the gas and press down on to the flame a piece of wire gauze (Fig. 59). What happens? Repeat the experiment with the air holes open. What difference does this make? Put out the flame, turn on the gas again and light it above the gauze (Fig. 60). Why does not the flame pass through?

Fig. 59.

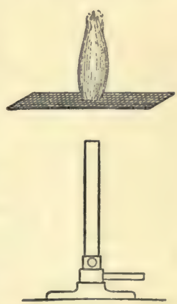

Fig. 60.

Ex. 128.—Set fire to a little methylated spirit in a basin, hold the basin with the tongs, and pour the burning liquid through a piece of wire gauze into another basin. Describe what happens?

128. Davy's Safety Lamp.—These experiments bring out the principle of the safety lamp invented in 1816 by Sir

Humphrey Davy to prevent explosions in coal mines. These explosions are caused by the presence of "fire damp," or marsh gas, which escapes from fissures in the coal and forms with the air in the mine an explosive mixture. Davy's safety lamp (Fig. 61) is simply an ordinary lamp surrounded by a cylinder of wire gauze. When it is brought into a mixture of coal-gas and air, the explosive mixture burns inside the lamp (thereby warning the miner of his danger); but the flame cannot pass through the gauze, since in doing so the gas would be cooled below its ignition point, and no explosion takes place.

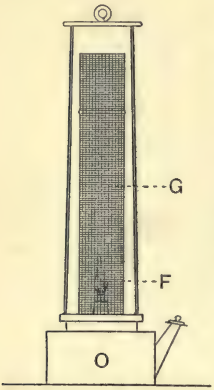

Fig. 61.

Ex. 129.—Take a cork, 3 to 4 cm. in diameter, and a piece of fine brass wire gauze, 12 cm. square. Roll the gauze into a cylinder of such diameter that the cork will fit tightly into one end of it. Cut out of the same wire gauze a circle, a little larger in diameter than the cylinder. Draw out four or five of the bent wires at the top of the cylinder, so that the straight wires are left projecting free for 5 or 6 mm. Cover the top of the cylinder with the circle, passing the straight wires through the gauze near the edge of the circle, and fixing them by bending them over. Now fix a small candle to the cork, by melting the wax at the bottom. Light the candle, slip the wire gauze cylinder over the cork, and the safety lamp is complete. To show its action, pass a little coal-gas up into a wide-mouthed bottle or jar, so as to form an explosive mixture. Now pass the safety lamp (which may be held by a wire pushed into the cork) up into the jar. Notice what happens. Afterwards put a naked flame up into the jar to convince yourself that the gas was inflammable.


Fig. 62.

129. Products of Combustion. — In all ordinary cases of combustion the products are carbon dioxide and steam. Although quite invisible, these products, of course, weigh much more than the original substance which was burned. This can easily be shown to be the case, if we burn a candle under a tube containing solid caustic soda, which will absorb and retain both the carbon dioxide and the steam given off from the flame.

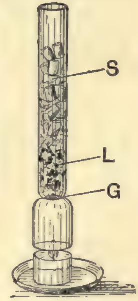

Fig. 63.

Ex. 130.—Take a straight lamp-glass having a contraction near one end (see Fig. 63). Put into it a small circle of wire gauze, just wide enough to be stopped by the contraction. Above this put a layer of quicklime in large lumps, and then a layer of caustic soda in sticks about 2 cm. long. Hang the whole arrangement to one hook of the balance,[1] and under it, on the pan of the balance, place an ordinary night-light. Counterpoise the whole carefully by weights. Then light the candle and let it burn for a few minutes. You will find that there is a considerable increase of weight. Where does the increase come from? Remember that this experiment does not in any way contradict the principle of the indestructibility of matter. Had we weighed all the substances taking part in the action, before and after it, we should have found no change: but we did not do so. Which did we leave out at the first weighing?

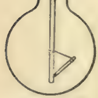
Fig. 64.

Ex. 131.—Take a round-bottomed flask of at least a ½ litre capacity. Fit it with an india-rubber stopper, through which passes a thin-walled glass tube closed at one end and of about 4 mm. bore. The closed end of the tube should reach nearly to the bottom of the flask. By means of wire, fix a wax match [2] so that its head touches the tube near the closed end, while its other end projects obliquely upwards (see Fig. 64). Put the stopper in tightly, and weigh the whole

[1] If the balance is too small to allow of this, the lamp-glass and the night-light should be weighed (separately) before and after the combustion.
[2] It is best to cut away half of the head and tease out the cotton beside the remaining portion with a pin to ensure its taking fire.

apparatus carefully. Now take a slender glass rod thin enough to enter the tube freely. Heat one end of it in the flame, and pass it down the tube to where the head of the match is placed. The match will take fire and burn so long as the supply of oxygen in the flask holds out. Allow the apparatus to become *perfectly* cold and weigh again. Do you find any alteration? Loosen the stopper and weigh again. What do you find?[1] Explain your results.

130. Composition of Food Stuffs.—Ex. 132.—Put some bread crumbs into a porcelain basin supported on wire gauze and heated by a small flame, until a dry watch-glass is no longer dimmed when held over the mouth. Now put two or three crumbs of the dried bread into a dry test-tube and heat it strongly. What happens? Test the liquid which condenses in the cold part of the tube with litmus paper. Now fit the test-tube with a doubly bored cork, and pass oxygen from a gas holder into it, continuing at the same time to heat it (Fig. 65). Pass the gas that issues from the test-tube into another tube containing clear lime-water. A white precipitate is formed. What does this prove as to the composition of bread?

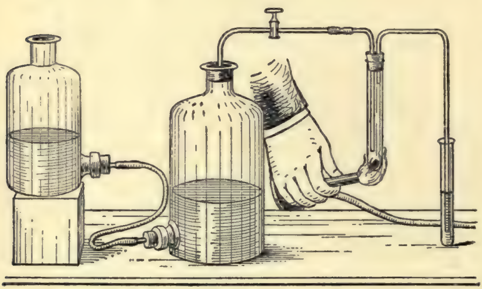

Fig. 65.

Ex. 133.—Repeat the last experiment with sugar, potatoes, lean meat, and cheese, the three last substances being first dried so as to expel most of the water which they contain. What resemblances and differences do you find?

131. All Food Stuffs contain Carbon.—The result of these

[1] This experiment is more convincing if some oxygen be first introduced into the flask, as in that case a much larger portion of the wax is burned away.

and hundreds of similar experiments may be summed up as follows:—

(1) All food stuffs contain carbon, most of which, as a rule, is left behind in the form of charcoal when they are heated out of contact with the air.

(2) They also contain hydrogen and oxygen, for all give *water* when heated (this is in addition to the water which exists in the food as such and can be driven off by heating to 100° C.).

(3) Those of animal origin (except fat) also contain nitrogen, for they give off ammonia when heated, and ammonia contains nitrogen (see pp. 90 and 160).

132. What becomes of all the Carbon which we take into our Bodies?—If we compare the amount of food which we consume with the amount which passes from the body in the form of visible waste products, we shall find there is a large proportion unaccounted for. Where does the excess go to?

The following experiments supply the answer.

Ex. 134.—Blow air from the lungs through a glass tube dipping into some clear lime-water in a test-tube. The lime-water immediately becomes milky.

Ex. 135.—Collect some air from your lungs in a wide test-tube over water. Use the last portion expelled when the lungs are nearly empty. Test it with a lighted taper. The taper will be extinguished.

Ex. 136.—Take a long tube closed at one end, such as was used in Ex. 33. Pass a narrow glass tube to the bottom of it and blow through this so as to fill the wider tube with expired air from the lungs. Withdraw the narrow tube, and quickly close the other with the thumb, and place it mouth downwards in the pneumatic trough. Now wrap a small piece of caustic soda (about 5 gm.) in thin paper, and pass it quickly up into the tube, and at once close the latter with the thumb, which had better be protected by an india-rubber finger-stall. Shake well, open under water (but do not let the undissolved caustic soda drop out), shake up again, and mark with an india-rubber ring the level to which the water rises when the tube is again placed with its mouth under water and the thumb is loosened. Now insert in the same way as the caustic soda

about 1 gm. of compressed pyrogallic acid, shake thoroughly for some time, and again mark the level of the liquid when no further contraction occurs. Now find (1) the volume of gas originally taken, (2) the contraction on shaking with caustic soda—that is, *the carbon dioxide contained* in it, (3) the contraction on shaking with caustic soda and pyrogallic acid—that is, *the oxygen contained* in it.

It will be found that the air "expired" or breathed out from the lungs contains about 3 °/ₒ by volume of carbon dioxide, and only about 18 °/ₒ of oxygen. Ordinary air contains only about ·04 °/ₒ of carbon dioxide, so that almost the whole of the three per cent. found in expired air must have come from within the body.

Ex. 137.—Find, by breathing through a *wide* tube and collecting and measuring the air, about what volume of air is expelled from your lungs at each breath. Find also how many times you breathe in a minute. Calculate from this, and from the results of the last experiment, how many litres of carbon dioxide you manufacture in twenty-four hours. Assuming that one litre of carbon dioxide at ordinary temperature weighs 1·9 gm., what will this number of litres weigh? and what weight of carbon does it contain?

If you make no mistake, you will probably find that you convert each day nearly half-a-pound of carbon into carbon dioxide. This carbon, of course, must come from the food which you consume, and in combining with oxygen it gives out a great deal of heat. It is the heat produced in this chemical action that causes your body to have a temperature higher than that of your surroundings, so that it may be compared to a steam engine, and the food you eat to the fuel with which the furnace is fed. In both cases the combustion of carbon compounds is the main source of energy; and in both cases some of this energy—more or less according to the efficiency of the engine, and the habits of the person—is converted into mechanical work.

133. Why does the Composition of the Atmosphere remain constant?—Since the carbon dioxide produced by the respiration of animals, and still more that formed by the combustion of fuel, must amount in the aggregate to thousands of tons per day, it may be asked why the proportion of carbon dioxide in

the atmosphere does not increase. It is not found to do so. It remains constant at ·04 per cent. The following experiments supply the answer to the question.

Ex. 138.—Fill a bottle (Fig. 66) with air from the lungs. Test it with a taper to make sure that it contains a sufficien proportion of carbon dioxide to extinguish a light. Now put into the bottle some freshly-cut leaves from a young and vigorous plant. Put in the stopper tightly and expose the whole to bright daylight—direct sunshine if possible—for an hour or two. Remove the leaves and test the air with a lighted taper. You will find that the taper burns as in ordinary air. The experiment shows that the carbon dioxide which is constantly being given off into the atmosphere is removed from it again by the agency of living plants. It is found that this action takes place only in daylight, and is only brought about by the green parts of plants. If the bottle be placed, mouth downwards, over mercury, it is found that no alteration takes place in the volume of the air. Hence it appears that the carbon dioxide is not absorbed as a whole, but that the plant is able to take out and retain the carbon, setting free the oxygen, which, as we know from Ex. 109, occupies the same bulk as the original carbon dioxide.

Fig. 66.

134. Plants breathe out Oxygen when exposed to Daylight.—That oxygen is given off may be shown directly by experiment.

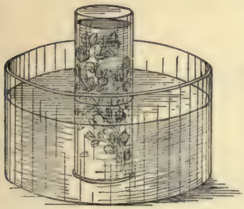

Fig. 67.

Ex. 139.—Fill a tall jar or beaker with water saturated with carbon dioxide, put into it some fresh water-cress or duckweed[1] and invert it in a basin of water. Leave the whole exposed to bright sunlight. Bubbles of gas are gradually given off from the cut stems and collect at the top of the jar. The gas when transferred to a narrow tube and tested is found to relight a glowing splinter.

[1] If these cannot be got, land plants (*e.g.* chrysanthemum leaves) may be used. But in this case a day or two may be required before sufficient oxygen is collected.

135. Mutual Dependence of Plants and Animals.—The fact that the proportion of carbon dioxide in the air remains constant at about ·04 % shows that the two sets of actions—that of animals and of combustion in contaminating the air with carbon dioxide, and that of plants in purifying it again—exactly balance each other. We see, too, that carbon is essential to the life of both plants and animals, and that the whole stock of carbon that exists in the world is constantly going through a cycle of changes from carbon dioxide to starch, sugar, etc., in the tissues of plants—from these, again, to still more complex compounds in the bodies of animals—and thence, partly by the vital process of respiration, partly by death and decay, back into the atmosphere in the form of carbon dioxide once more. Notice that while plants could exist perfectly well without the presence of animals, the animals are entirely dependent upon living plants for their existence; for not only do all animals feed either upon plants or upon other plant-eating animals, but they cannot exist in an atmosphere containing more than a small proportion of carbon dioxide, and this proportion would in the course of time be reached and all animal life consequently destroyed, were it not for the action of plants in removing it and replacing it by oxygen.

QUESTIONS AND EXAMPLES ON CHAPTER XII.

1. How would you prove the presence of carbon in the following substances;—sugar, cheese, starch, diamond?

2. What is meant by the Law of Multiple Proportions? Give three examples.

3. Copper forms two oxides. One gramme of the first, when heated in hydrogen, leaves 0·797 gm. of copper; one gramme of the second, under the same conditions, gives 0·887 gm. of copper. Show that these results agree with the Law of Multiple Proportions.

4. Calculate the percentage composition by weight of the two oxides of carbon.

5. Explain the principle of the Davy lamp. Why is it dangerous for a miner to leave such a lamp in a rapid current of air, where the flame may be blown against the wire gauze?

6. 1 gramme of a certain substance, when burned in oxygen, yielded

3·438 gm. of carbon dioxide and 0·563 gm. of water. Calculate the percentages of carbon and hydrogen which it contains.

7. Describe with sketch an experiment to show that when a candle burns the products of combustion weigh more than the original candle.

8. Explain with a sketch the construction of the Bunsen burner. How do you account for the fact that the flame becomes larger as the air-holes at the bottom are made smaller?

9. What is the use of the wick in an ordinary candle? Why is the wick made so that it bends to one side as the candle burns?

10. If it were possible to live in an atmosphere of hydrogen, what substances would we use to make fires with?

11. Explain the action of plants and animals upon the air.

12. Write the equation for the action that takes place when black oxide of copper (CuO) is heated in carbon monoxide. What weight of the oxide could be completely reduced by 10 litres of the gas? (Density of carbon monoxide $= 14$.)

CHAPTER XIII

ALKALIES, ACIDS, AND SALTS

136. Alkaline Substances.—We have already seen that most of the substances which have alkaline properties—*i.e.* which turn red litmus blue and yellow turmeric brown, and which combine with acids—belong to the class of hydrates of the metals; that is, they are compounds of a metal with oxygen and hydrogen, like calcium hydrate or slaked lime.

137. Caustic Soda. — The most important of these substances is caustic soda or sodium hydrate, which has the composition expressed by the formula NaOH, and can be got by the direct action of sodium upon water, thus

$$Na + H_2O + NaOH + H$$

or by burning sodium in the air and adding water to the oxide. Both these methods are expensive, for metallic sodium is difficult to prepare, and therefore commands a high price. A cheaper plan is to start with "soda ash" or sodium carbonate, which was formerly obtained from the ashes of seaweed, but is now made in enormous quantities from common salt.

Ex. 140.—Dissolve 5 gm. of anhydrous sodium carbonate in about 100 c.c. of hot water. Take 10 gm. of freshly burned quicklime and slake it with 50 c.c. of hot water in a porcelain basin. Add the sodium carbonate solution, stir well, and boil for quarter of an hour. Filter a few drops of the liquid into a test-tube and add hydrochloric acid. If there is no effervescence the reaction is complete. Pour the milky liquid into a tall jar and leave it to settle. Then draw off and evaporate the clear liquid in a porcelain or nickel basin and compare the residue with that obtained in Ex. 40. Test the insoluble residue left in the jar by filtering and adding hydrochloric acid to a little of it. Does it effervesce? What, tnen, is the reaction that has taken place?

Caustic soda or sodium hydrate is made on a large scale by the process used in this experiment and is employed for making soap, for removing grease and other impurities from cotton cloth, and for many other purposes. It quickly destroys the skin, and in fact all animal tissues — hence the name caustic (= burning).

138. **Caustic Potash.**—The corresponding potassium compound is called caustic potash or potassium hydrate. It may be made by exactly the same methods that are used for the preparation of sodium hydrate, the raw material being in this case potassium or potassium carbonate. The latter substance is still obtained to some extent from wood ashes, which were formerly the only source of supply. Hence its old name of "potashes," from which potassium is derived. The formula of potassium hydrate is KOH, and it is used for the same purposes as sodium hydrate, but on a smaller scale, as it is more expensive. The equation for the reaction by which it is prepared is

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3$$

139. **Slaked lime** and **Magnesium hydrate** are also included in the list of alkalies. They resemble the hydrates of sodium and potassium in their general properties, but differ markedly from them in being only sparingly soluble in water and also in being decomposed by heat, whereas potassium and sodium hydrates are very easily soluble and are not broken up by heat.

140. **Other Metallic Hydrates.**—Most other hydrates of metals are insoluble in water and have no alkaline properties, *i.e.* they do not act upon litmus or turmeric, nor do they destroy animal tissues, like caustic soda, potash and lime. But they are like the alkalies in this — they combine with acids in the same way to form salts.

Ex. 141.—Add some caustic soda or potash solution to a cold solution of copper sulphate. Filter off and wash the precipitate produced. Find out the action upon it (*a*) of heat, (*b*) of nitric acid, (*c*) of sulphuric acid.

The reaction that takes place in this experiment is represented by the equation

$$CuSO_4 + 2KOH = K_2SO_4 + Cu(OH)_2$$

Most of the other metallic hydrates are got by double decomposition from a salt, just as in this case. With few exceptions they behave to acids like calcium or copper hydrate, combining with them to form a salt and water, thus:

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O$$
$$Cu(OH)_2 + H_2SO_4 = CuSO_4 + 2H_2O$$
$$Zn(OH)_2 + 2HNO_3 = Zn(NO_3)_2 + 2H_2O$$

They also combine directly with carbon dioxide and sulphur dioxide to form carbonates and sulphites.

141. The "Volatile Alkali."—Besides the three alkalies already named, there is another common alkali which is in many respects so entirely different from them that it must be put into a class by itself. This substance is ammonia, or, to give it its old-fashioned name, "spirits of hartshorn."

Ex. 142.—Put a few clippings of horn into a dry test-tube, and heat them. Notice the odour which is given off. Try the effect of the fumes upon litmus and turmeric papers.

Ex. 143.—Repeat the last experiment, but mix the clippings with powdered caustic soda before heating. Hold a glass rod, the point of which has been dipped in strong sulphuric acid, in the mouth of the tube for a minute or two. What happens to the acid when the glass rod cools?

The gas which is given off in the last two experiments is ammonia gas—the same gas that is formed in small quantity by the destructive distillation of coal. The latter substance is the chief source of ammonia, for although the quantity of ammonia got from a ton of coal is only a few pounds, the quantity of coal distilled for the manufacture of gas and coke is so enormous that this gives in the aggregate a very large quantity of ammonia.

142. Preparation of Ammonia.—In the laboratory ammonia is usually prepared by heating sal ammoniac with quicklime.

Ex. 144.—Powder a few grammes of quicklime in a mortar, and mix it quickly with about half its bulk of sal ammoniac. Put the mixture into a wide test-tube, fitted with a cork and leading tube, support this in a nearly horizontal position, with the mouth slightly lower than the other end of the tube, and collect the gas by upward displacement in *dry* bottles or test-

tubes (see Fig. 68). Place one of these with its mouth under water—what happens? Is the gas much lighter than air? Does it burn or support combustion? What happens when a glass rod dipped in (*a*) strong sulphuric acid, (*b*) strong hydrochloric acid, (*c*) strong nitric acid is put into a jar of the gas? [The action of water upon the gas may be shown more strikingly by the apparatus shown in Fig. 69. The bottle is dried and filled by displacement with ammonia, then closed by a cork through which passes a glass tube drawn out to a fine jet. On putting the end of this tube under water (which may be reddened by the addition of a little litmus and a drop of dilute acid) and then cooling the jar by pouring cold water on it, the water will form a fountain inside the bottle, and the colour of the litmus will be changed to blue.]

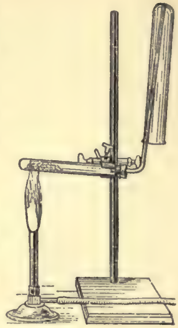

Fig. 68.

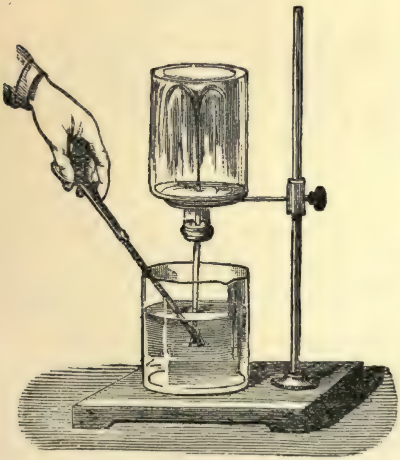

Fig. 69.

143. Composition of Ammonia.—These experiments will have shown you the chief properties of ammonia gas. The fact that the gas shows some tendency to burn gives a clue to its composition. If we heat the tube from which it is issuing, or surround it with oxygen, the gas burns readily enough; and by holding over the flame a cold glass vessel, it is easy to show that water is formed by the combustion. For this experiment the ammonia gas must be dried. Obviously this cannot

be done by the use of sulphuric acid, since the gas instantly combines with this and other acids to form solid compounds. Nor can calcium chloride be used, for with this also ammonia forms a compound. Quicklime is the best drying agent. In order to find out the composition of the gas it is burned by passing it over heated copper oxide, when the hydrogen which it contains is converted into water.

Ex. 145. — Fit up the apparatus shown in the figure. Ammonia gas is made by *very gently* heating some strong ammonia solution contained in the flask *A*, which rests on a sandbath. The gas passes through the weighed tube *T*, which contains partially oxidised copper wire gauze, and

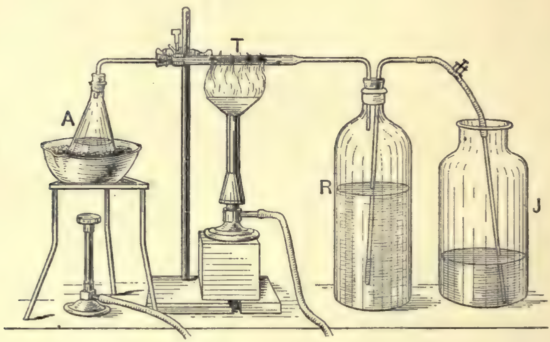

Fig. 70.

then into the reservoir *R*. The latter contains water, which dissolves any unchanged ammonia, while any insoluble gas that may be formed will expel its own volume of water from *R* into the jar *J*. By weighing the tube *T* after the experiment we can find how much oxygen has been used up in burning the hydrogen, and from this we can calculate the weight of hydrogen that has been burned (since we know that oxygen always combines with one-eighth of its own weight of hydrogen). The gas in *R* is found to be nitrogen, and from its volume and the volumeter reading we can calculate its weight.

It is found that ammonia gas consists of 14 parts by weight

of nitrogen, combined with 3 of hydrogen. Its composition is therefore expressed by the formula NH_3.

144. Synthesis of Ammonia from its Elements.—Nitrogen and hydrogen do not readily combine with each other directly; but ammonia can easily be prepared from them by an indirect method. When magnesium is heated in nitrogen, the two elements combine to form magnesium nitride. When this compound is acted on by water it is decomposed as follows:—

$$Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$$

In performing Ex. 68 some magnesium nitride is usually formed, and in consequence, as has already been noted, a little ammonia is given off when the residue of magnesia is moistened.

145. Action of Ammonia on Acids.—As we have seen, ammonia combines directly with acids. In each case *a single compound* is formed, not two, as with caustic potash and other alkalies. When a jar of dry ammonia gas and one of hydrochloric acid gas are brought mouth to mouth, and the glass plates which separate the gases are removed, combination takes place with the evolution of much heat. Dense white fumes are formed, which gradually settle down into a white snow-like powder of ammonium chloride or sal ammoniac — the substance which we used in Ex. 144. By performing this experiment over mercury it can be shown that the two gases combine in equal proportions by volume. Since the density of ammonia gas is 8·5, and that of hydrochloric acid is 18·25, it follows that the relative weights which combine are also in these proportions, and the reaction is therefore expressed by the equation—

$$\begin{array}{ccccc} HCl & + & NH_3 & = & NH_4Cl \\ 36{\cdot}5 & + & 17 & = & 53{\cdot}5 \end{array}$$

With sulphuric acid and nitric acid, the reactions are similar—

$$HNO_3 + NH_3 = NH_4NO_3$$
$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4$$

The salts thus produced by the union of ammonia with acids resemble pretty closely the salts of potassium and

sodium. Thus ammonium chloride is a white crystalline salt, easily soluble in water, and having a taste not unlike that of common salt.

Ex. 146.—Add a few drops of strong sulphuric acid to some ammonium chloride in a test-tube. What happens? Compare the result with that obtained by adding sulphuric acid to common salt. Heat the residue till no more fumes are evolved. What do you find?

146. Action of Heat on Ammonium Salts.—Ex. 147.—Heat small quantities of the following ammonium salts separately in test-tubes, and observe what happens in each case:—ammonium chloride, ammonium sulphate, ammonium nitrate, ammonium phosphate.

The fact that all ammonium salts are volatilised by heat gives us an easy means of distinguishing them from the salts of potassium and sodium. In some cases the ammonium salt when heated simply splits up into ammonia gas and the acid, and these recombine on cooling, so that we get the original substance practically unchanged. In other cases the salt is broken up into entirely new substances. As a rule, no residue is left in the crucible when any ammonium salt is heated. But in case the acid from which the salt was formed is not volatile at a red heat, it may remain behind as a residue. (Try to find out what happens in each of the cases given in Ex. 147.)

147. Ammonium Hydrate.—If you compare the formulæ of the potassium and sodium salts with those of the salts formed by the union of ammonia gas with acids, you will see that in the latter the group NH_4 (*i.e.* 14 parts by weight of nitrogen combined with 4 of hydrogen) takes the place of one combining weight of potassium or sodium. This group, which plays the part of an equivalent quantity of a metal, has been given the name "ammonium," as if it were really a metal,[1] and the salts formed by the union of ammonia gas with hydrochloric acid, nitric acid, and sulphuric acid are called ammonium chloride, ammonium nitrate, and ammonium sulphate respectively. Following the same analogy, the solution of ammonia gas in water is called ammonium hydrate, since it behaves in many respects exactly like a solution of caustic potash or soda. The formula $(NH_4)OH$ is

[1] Names ending in *um* are usually reserved for metals.

given to it, corresponding to KOH and NaOH ; but the existence of this compound is merely hypothetical — it has never been obtained in the pure state. If we evaporate its solution in the hope of doing so it at once splits up into ammonia gas and water—

$$(NH_4)OH = NH_3 + H_2O$$

148. Action of Alkalies on Ammonium Salts.—We have seen that ammonia gas is given off when sal ammoniac is heated with lime. All ammonium salts give the gas when treated with alkalies, whether lime, caustic soda, caustic potash, or even magnesia. In most cases it is not even necessary to heat the mixture. The alkali combines with the acid of the ammonium salt, and ammonia gas and water are set free. This reaction gives us a convenient method of testing for the presence of ammonium salts. We have only to mix the supposed ammonium salt with a little powdered quicklime in a small beaker, moisten the mixture with a few drops of water, and cover the beaker with a watch-glass to the under side of which a piece of moist turmeric or red litmus paper has been stuck. If the original substance contained ammonium the smell of ammonia gas will be perceptible in a minute or two, and the turmeric paper will be turned brown or the red litmus paper blue.

149. Relation of Acids to Alkalies.—From what has been said, you will see that all the alkalies (except ammonia) are compounds of metals with oxygen and hydrogen—or *hydrates* of metals. Many of the acids, as we have already seen, are also hydrates, but hydrates in this case of *non-metals*. There are some acids, however, like hydrochloric acid and hydrosulphuric acid (sulphuretted hydrogen), which are not hydrates, but compounds of a non-metal with hydrogen alone. All are alike in one respect—they *contain hydrogen which can be easily replaced by metals.*

When an acid and an alkali are brought together combination always takes place, and a compound called a *salt* is produced. We have had examples of this in Exs. 85 and 99. (What else is formed besides the salt?)

150. Salts.—These compounds may be produced, as we

have already seen, in several different ways. Some of the most important are—

(1) By the action of acids upon metals—*e.g.*

$$Mg + H_2SO_4 = MgSO_4 + 2H$$

(2) By the action of acids upon hydrates or oxides of metals—

$$MgO + H_2SO_4 = MgSO_4 + H_2O$$
$$Mg(OH)_2 + H_2SO_4 = MgSO_4 + 2H_2O$$

(3) By the action of acids upon metallic salts, especially carbonates and sulphides—

$$MgCO_3 + H_2SO_4 = MgSO_4 + H_2O + CO_2$$
$$MgS + H_2SO_4 = MgSO_4 + H_2S$$

(4) By the combination of an acid-forming oxide with a basic oxide—

$$MgO + SO_3 = MgSO_4$$

(5) By the direct union of a non-metal with a metal—

$$Mg + 2Cl = MgCl_2$$

Here is a list of some of the salts that have been formed in the experiments already described.

	Chloride.	Carbonate.	Nitrate.	Sulphide.	Sulphate.
Potassium .	KCl	K_2CO_3	KNO_3	...	K_2SO_4
Sodium .	$NaCl$	Na_2CO_3	...	...	Na_2SO_4
Silver . .	$AgCl$	...	$AgNO_3$	Ag_2S	Ag_2SO_4
Ammonium	$(NH_4)Cl$	...	$(NH_4)NO_3$	...	$(NH_4)_2SO_4$
Zinc . .	$ZnCl_2$	...	$Zn(NO_3)_2$	...	$ZnSO_4$
Magnesium	$MgCl_2$	$MgCO_3$	$Mg(NO_3)_2$	...	$MgSO_4$
Calcium .	$CaCl_2$	$CaCO_3$	...	...	$CaSO_4$
Copper . .	$CuCl_2$	...	$Cu(NO_3)_2$	Cu_2S	$CuSO_4$

It will be seen from the formulæ that all these salts are derived from the corresponding acids by the replacement of hydrogen by an equivalent quantity of a metal. Most of these salts are neutral to litmus, but a few are alkaline, and some are acid. Generally speaking, the salts of potassium, sodium, calcium, and magnesium with sulphuric, nitric and hydrochloric

acids are neutral, or have no action upon litmus. On the other hand, the carbonates of sodium and potassium, as we have seen, are alkaline; while most of the soluble salts of the heavy metals (such as zinc, copper, lead, etc.) are acid to litmus.

151. Alkalimetry.—In the case of salts which are *neutral* to litmus or other "indicators," their composition can be very quickly and easily found by measuring the *volume* of an acid solution of known strength which is required to exactly neutralise a certain weight of the oxide or carbonate of the metal. Suppose, for example, that we wish to find the composition of potassium chloride. We begin by making a solution of hydrochloric acid of known strength (a "standard solution"). This might be made to contain exactly ·01 gm. of real hydrochloric acid in 1 c.c. If now we weigh out exactly one gramme of pure caustic potash, dissolve it in water, add litmus, and then run in the standard hydrochloric acid from a burette until the colour of the litmus just changes from blue to purplish red, we can find by a simple calculation what weight of hydrochloric acid has united with one gramme of caustic potash. Suppose that 65·2 c.c. of the acid solution is required. The weight of real hydrochloric acid in this volume of solution is $65{\cdot}2 \times {\cdot}01 = {\cdot}652$ gm., and this weight of hydrochloric acid has united with one gramme of caustic potash. An easy calculation shows that in the same proportion one combining weight of hydrochloric acid (36·5 parts by weight) would have combined with 56 parts by weight of potassium hydrate. The reaction must therefore be

$$\begin{array}{ccccccc} HCl & + & KOH & = & KCl & + & H_2O \\ 36{\cdot}5 & + & 56 & = & 74{\cdot}5 & + & 18 \end{array}$$

This might be confirmed by evaporating down and weighing the potassium chloride produced. The equation being once known, we might use this method to find how much caustic potash is contained in a given weight of a solution or of a commercial sample.

EX. 147.—Take a light flask of about 200 c.c. capacity, with a tight-fitting india-rubber stopper. Put into it about 100 c.c. of distilled water, insert the stopper, and weigh the whole as accurately as possible. Now fit up the apparatus for making hydrochloric acid

gas (see Ex. 75). Push a loose plug of cotton-wool up into the end of the delivery-tube and insert it into the neck of the weighed flask, taking care that the tube does not touch either the water or the sides of the flask. The flask should stand in a shallow basin of water, so that it may be kept quite cold during the absorption of the gas. Now send a fairly rapid stream of hydrochloric acid gas into the flask for twenty minutes or half-an-hour. Remove the delivery-tube, insert the stopper in the neck of the flask, dry its outside carefully, and allow it to cool. Take out the stopper for a moment, replace it, and find the weight of the flask with its contents. The increase over the original weight gives, of course, the weight of hydrochloric acid gas which has dissolved in the water. Now take a litre flask, put a funnel into the neck, and pour in the acid from the weighed flask, having first diluted it with some distilled water in case it shows any tendency to give off fumes in the air. Fill up the small flask with distilled water three or four times, each time emptying it into the large flask and taking care not to lose a single drop of the liquid. Wash into the funnel by means of the wash-bottle any acid that remains about the neck of the small flask or in the funnel. Now fill up the litre flask with distilled water exactly to the mark on the neck, insert the stopper and shake for some time, inverting the flask several times so as to mix the liquid very thoroughly. The standard solution is now ready and may be transferred to a bottle and labelled with the weight of real hydrochloric acid contained in 1 c.c., which will of course be one-thousandth part of the total weight of hydrochloric acid gas taken. In transferring the solution to the bottle (and afterwards to burettes, etc.) remember that the latter must either be quite dry or must first be rinsed out with a few c.c. of the solution, which is then thrown away. If this precaution be neglected the strength of the acid solution will be altered and the results got by its use will be unreliable.

Ex. 148.—Weigh out accurately about 3 gm. of anhydrous sodium carbonate, dissolve it in distilled water in a 250 c.c. flask, and make up the solution exactly to the mark on the neck of the flask with distilled water. Mix the solution well, take out 10 c.c. by means of a pipette, and transfer it to a small beaker or "beaker flask." Add one or two drops of a weak solution of methyl orange [1]—just sufficient to give a very faint yellow tint to the solution. Fill a clean dry burette with the standard acid, and run out some till the zero mark is reached. Now run the acid slowly into the sodium carbonate solution, stirring all the time, until the colour just changes from yellow to pink. A single drop of the acid ought to be sufficient to bring about the change. Having now found the

[1] This is a dye-stuff which is yellow in alkaline solution and pink in presence of acids. It has the advantage, as compared with litmus, of being unaffected by carbonic acid.

volume of acid required to neutralise 10 c.c. of the sodium carbonate solution, a more exact result will be got by repeating the experiment with a larger volume—say 50 c.c. Suppose that in the first experiment 6 c.c. of standard acid was used. If this result were *exactly* correct, 50 c.c. should require exactly five times as much, or 30 c.c. But in all probability the first result was too high, for it is difficult to hit the exact point of neutrality, and moreover a certain volume of acid—say $\frac{1}{10}$ c.c.—is required to act upon the methyl orange and bring about the change of colour. This quantity is about the same whether we use 6 c.c. of the acid solution or 30 c.c. But it is evident that while an error of $\frac{1}{10}$ c.c. in a total of 6 c.c. is comparatively large (nearly two per cent.), an error of the same amount in a total of 30 c.c. is only one-fifth as great. (The principle is the same that has already been pointed out in the note on p. 74.) Therefore take 50 c.c. of the sodium carbonate solution, add methyl orange as before, and run in quickly 26 or 27 of the standard acid. Then continue to add it drop by drop until the exact point of neutrality is reached.[1] Read off the number of c.c. used, multiply it by the weight of real HCl in 1 c.c., and so find what weight of hydrochloric acid is required to neutralise the sodium carbonate contained in 50 c.c. of the solution, which will, of course, be one-fifth of the total weight of carbonate originally weighed out.

The result of the last experiment should agree with the equation

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$

Compare it with that which you obtained in Ex. 111.

152. "Washing Soda" and "Baking Soda."—The two forms in which sodium carbonate is familiar to everyone are "soda crystals" or "washing soda," and "baking soda" or "bread soda," the "bicarbonate of soda" of the druggist. These two substances are typical of two different classes of salts, and it will be useful to study their composition and the relation between them.[2]

[1] It is a very common practice in experiments such as this to make a large number of determinations with the same volume of solution, which is frequently chosen so that only 4 or 5 c.c. of the standard solution are used in each experiment. Such a procedure is a stupid waste of time, for all the results will be equally unreliable. At most three experiments should suffice—a preliminary rough experiment with a small volume of the solution, and one or two accurate experiments, with a larger volume, chosen so that at least 25 or 30 c.c. of the standard solution may be used.

[2] The experiments which follow are repetitions or applications of others that have already been performed. They should therefore be distributed among the class, one group being set to work out Ex. 149, another to Ex. 150, and so on.

Ex. 149.—Take some "soda crystals," powder them, and heat a little of the powder in a dry test-tube fitted with a leading tube which dips into water. Is any gas given off? Is anything else? Examine the substance that remains behind. Does it effervesce with acids? Is it alkaline? Find out by repeating Ex. 110, or Ex. 148, whether it is ordinary anhydrous sodium carbonate.

Ex. 150.—Determine the loss of weight that occurs when soda crystals are heated in a covered crucible till the weight remains constant. (Use 1 to 2 gm.) Calculate what weight of soda crystals would leave one combining weight (106 parts by weight) of anhydrous sodium carbonate. Dissolve the residue in the least possible quantity of boiling water, and allow the solution to stand. What happens?

It appears from these experiments that "soda crystals" or "washing soda" is simply ordinary soda ash or sodium carbonate combined with water of crystallisation. The proportion of water is unusually large, the formula being $Na_2CO_3,10H_2O$—*i.e.* 106 gm. of sodium carbonate unites with 180 gm. of water.

Let us next make similar experiments with "baking soda."

Ex. 151.—Repeat Ex. 149, using bicarbonate of soda. What do you find?

Ex. 152.—Heat a weighed quantity of the pure bicarbonate in a crucible. Calculate what weight of bicarbonate would give 106 gm. of residue. What weight of carbon dioxide is present in this residue?

Ex. 153.—Find by the method used in Ex. 54 what weight of carbon dioxide is contained in one gramme of the bicarbonate, and hence the weight of carbon dioxide contained in one combining weight of the bicarbonate (*i.e.* the weight of bicarbonate, which leaves behind 106 gm. of sodium carbonate when heated). What is the relation between (1) the total weight of carbon dioxide in a given weight of bicarbonate, and (2) the weight of carbon dioxide in the residue left after heating?

The results of these experiments will show (1) that bicarbonate of soda, when heated, gives off water *and carbon dioxide* (2) That the residue which remains after heating is ordinary sodium carbonate, Na_2CO_3. (3) That the carbon dioxide which can be driven off by heat is equal in amount to that

which remains behind in the residue of Na_2CO_3. (This is determined by subtracting the weight of carbon dioxide present in the residue from the total amount present in the original bicarbonate, as determined in Ex. 153.) (4) That for every two combining weights of carbon dioxide (88 parts by weight) in the original bicarbonate, one combining weight of water (18 parts by weight) is given off on heating. In other words, 168 gm. of sodium bicarbonate, on heating, gives 18 gm. of water, 44 gm. of carbon dioxide, and 106 gm. of sodium carbonate. It follows that the formula of the bicarbonate may be written Na_2CO_3,H_2O,CO_2, or Na_2CO_3,H_2CO_3. The former indicates that bicarbonate of soda may be regarded as a compound of one combining weight of sodium carbonate, with one of carbon dioxide, and one of water. The latter represents it as a compound of one combining weight of sodium carbonate with one of the hypothetical carbonic acid, H_2CO_3. The action of heat upon the substance is thus expressed by the equation—

$$\begin{array}{ccccccc} Na_2CO_3,H_2CO_3 & = & Na_2CO_3 & + & H_2O & + & CO_2 \\ 168 & = & 106 & + & 18 & + & 44 \text{ parts by weight.} \end{array}$$

153. Acid Salts and Normal Salts.—There is still another way in which the formula of bicarbonate of soda may be written—viz. $NaHCO_3$. According to this the substance is a salt of carbonic acid, derived from the acid in the usual way, by replacing its hydrogen by the equivalent weight of metal. But in this case *only half of the hydrogen is replaced.* The product is therefore half acid, half salt. It is a salt because it is derived from an acid by replacement of hydrogen by a metal; it is an acid because it still contains hydrogen which can be replaced by metals. Thus, if it be treated with sodium hydrate (caustic soda), combination occurs according to the equation—

$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O$$

On the other hand, if soda crystals be treated with carbon dioxide, the gas is gradually absorbed, and the bicarbonate is formed. This is the process by which the bicarbonate is prepared on the large scale. Bicarbonate of soda or sodium hydrogen carbonate is a type of a large class of compounds known as **acid salts,** which, like it, are derived from acids by

replacement of only part of their hydrogen by metals. Salts which are formed by the replacement of *the whole* of the hydrogen of an acid by a metal are called **normal salts**, and most of the salts which we have prepared belong to this class. But the residue left after preparing hydrochloric acid gas from common salt and sulphuric acid is an acid salt—it is sodium hydrogen sulphate[1] or "acid sodium sulphate," $NaHSO_4$.

Ex. 154.—Dissolve some acid sodium sulphate[2] in a little water. Find out whether the solution acts upon litmus and upon sodium carbonate. Mix a little of the powdered crystals with an equal bulk of common salt, and heat strongly in a dry test-tube. What happens?

The results of these experiments show that acid sodium sulphate, though a salt, has also the properties of an acid, for it expels carbon dioxide from carbonates and hydrochloric acid gas from common salt.

The reaction that occurs in the preparation of hydrochloric acid gas is $NaCl + H_2SO_4 = NaHSO_4 + HCl$. At a much higher temperature (too high to be conveniently reached in a glass flask) the acid sodium sulphate acts upon a further portion of common salt; thus—$NaCl + NaHSO_4 = Na_2SO_4 + HCl$. In this case the acid salt ($NaHSO_4$) has an acid reaction to litmus, while the normal salt (Na_2SO_4) is neutral. But it is important to notice that this is not always the case. A salt may be an acid salt—*i.e.* may contain hydrogen that can be replaced by a metal—even though its action on litmus may be that of an alkali. Sodium bicarbonate is a case in point.

154. Salts present in Natural Waters.—Since nearly all salts are more or less soluble in water, it is not surprising to find that all natural waters contain salts in solution. The purest natural water is rain water, and this, if collected on a clean surface of metal or other insoluble material, contains only a trace of solid matter. River water contains dissolved solid matter in very various amounts, according to the kind of rocks over which the particular river runs. The water of many highland streams running through districts where granite is

[1] The name sodium bisulphate (corresponding to sodium bicarbonate) is not now used.

[2] The residue from Ex. 75 may be recrystallised from hot water, and the crystals dried by pressing them between blotting-paper.

the prevailing rock is nearly pure, while that of the more sluggish lowland rivers contains a comparatively large amount of salts in solution. Spring and well waters, having been in contact with a large surface of earth or rock for a long time, usually contain more solid matter in solution than river water, while sea water contains the most of all.

Ex. 155.—Find the amount of solid matter in any samples of water that may be available by evaporating 70 c.c. of the water in a weighed porcelain basin and weighing the dry residue. Since 70 c.c. of water weigh 70,000 mgm., and one gallon of water weighs 70,000 grains, the weight of the residue in milligrams will be equal to the number of grains that would be got by evaporating one gallon of the water.[1]

The following table shows the amount of dissolved salts in some typical waters :—

	Grains of dissolved solid matter in one gallon.
London (New River) . . .	17·6
Glasgow (Loch Katrine) . . .	2·3
Croydon (well water) . . .	23·3
River Irwell (above Manchester) . .	5·5
„ (below Manchester) . .	39·1
Irish Sea	2370·

155. Hard and Soft Waters.—River and spring waters are popularly classified into "soft" and "hard" waters. The former give a lather at once when shaken up with a little soap—the latter do not do so, but give a white curdy precipitate, and only produce a lather when a comparatively large quantity of soap has been dissolved. When hard water is used for washing, a great deal of soap is wasted in producing this curdy precipitate. Moreover, hard water when boiled gives a deposit of "fur" or "scale" on the bottom of the kettle or boiler. This deposit is a bad conductor of heat, and therefore leads to waste of heat and to overheating and consequent rapid oxidation of the metal of the boiler. For these reasons hard waters are never used for boilers or for washing when soft water can be got. The following experiments will bring out the cause of this remarkable difference between the behaviour of the different classes of water.

[1] The solid matter in water is usually stated as so many grains per gallon.

Ex. 156.—Prepare a solution of soap by dissolving 5 gm. of Castile soap in fine shavings in half a litre of dilute methylated spirit (one volume of spirit mixed with two of water). Fill a burette with the soap solution. Now take 20 c.c. of rain water or distilled water in a small stoppered bottle and find out what volume of soap solution must be added to it in order to give on shaking up a decided lather which will last for at least a minute. Repeat the experiment with a sample of hard water from a chalk or limestone district and note the result.

Ex. 157.—Put into a beaker 250 c.c. of the same hard water that was used in the last experiment. Boil it for twenty minutes or half-an-hour and make it up to the original volume by the addition of distilled water. Allow to cool, and measure out 20 c.c. by a pipette and find how much of the soap solution is now required to give a permanent lather. You will find that considerably *less* soap solution is required than was needed for an equal volume of the unboiled water.

These experiments will show that rain water is soft (as indeed we should expect, since it is a natural distilled water) and that water from chalk or limestone districts is very hard, but is more or less completely softened by boiling.

Ex. 158.—Evaporate 20 c.c. of the hard water to dryness on the water-bath, take a little of the residue left behind, put it on a watch-glass, and add to it a drop of hydrochloric acid. What happens? Heat a few grains of it on thin platinum (or iron) wire in the Bunsen flame. Place the residue on a piece of moist red litmus or turmeric paper. What do you find? Did the residue give the same result before heating? Dip your wire into the solution produced by the action of hydrochloric acid on the residue. Hold it in the lower edge of the Bunsen flame and note the colour which it imparts to the flame. Compare this with the colour given by a drop of the solution formed by dissolving chalk in hydrochloric acid

156. Hard Water leaves a Residue of Chalk when evaporated. — These experiments show that the residue left on evaporating hard water consists at least in part of *chalk*. But we know from Ex. 50 that chalk is practically insoluble in water. How, then, can it be present in the hard water, which is perfectly clear and free from sediment? The following experiment will give a clue to the answer.

Ex. 159.—Fill a small beaker or flask with the hard water and heat it on wire gauze over the flame. Notice very carefully what happens before and after boiling. Filter off, and test the precipitate which forms when the water boils. You will find that it is chalk. How do you account for the bubbles which rise to the surface and escape, *before the water boils*?

157. Water contains Dissolved Gases.—If we remember that all natural waters are more or less exposed to contact with the gases of the atmosphere, it will be readily understood that they must contain dissolved gases. Boiling the water, as we have seen, has the effect of expelling these gases, and also of causing a precipitate of chalk. Is it possible that there is a connection between the two things? The first step towards finding this out will be to investigate the composition of the dissolved gases.

Ex. 160.—Fit a flask of at least 1 litre capacity with a rubber stopper and a leading-tube. (See Fig. 71.) The leading-tube must not project below the surface of the stopper. Fill the flask to the brim with hard water and press in the stopper. This should have the effect of filling the leading-tube completely with the water. Now support the flask on wire gauze over a Bunsen burner and arrange to collect any gas that may be given off in a small narrow jar. Boil the water till no more gas is evolved, and find out what volume of gas is contained in 1 litre of the water. Now with the help of a funnel, transfer some of the gas to a narrow tube and find out exactly as in Ex. 136 what proportion of carbon dioxide, oxygen, and nitrogen it contains.

Fig. 71.

158. Action of Water containing dissolved Carbon Dioxide upon Chalk.—It will be found that the gas expelled from hard water by boiling contains a large proportion of carbon dioxide. If this has anything to do with the solubility of the chalk in the original water, it should be possible to

re-dissolve the chalk by shaking up the turbid water with carbon dioxide.

Ex. 161.—Take some of the turbid liquid formed on boiling the hard water, cool it thoroughly and pass a current of carbon dioxide into it, or blow air from your lungs through it for some minutes. Leave the solution to stand for twenty minutes. What happens?

Ex. 162.—Take 2 or 3 c.c. of lime-water, dilute it with three or four times its volume of distilled water, and blow air from the lungs through it. A precipitate of chalk will be formed. Continue to blow air through the liquid or pass a current of carbon dioxide into it. You will find that in a little while the precipitate will dissolve. On boiling it reappears.

If the results of these experiments be compared with those of our experiments on sodium carbonate and bicarbonate, it will be seen that the explanation of the formation of chalk on boiling hard water is quite easy. Chalk, the normal calcium carbonate, is insoluble in water. But when treated with carbonic acid (*i.e.* a solution of carbon dioxide in water) it is converted into an acid carbonate, exactly as normal sodium carbonate is converted into the bicarbonate. In the case of sodium, both carbonates, as we have seen, are soluble in water, the acid carbonate being the less soluble of the two. In the case of calcium, on the other hand, the acid carbonate only is soluble, the normal carbonate being quite insoluble in water free from carbon dioxide. In both cases the acid carbonate is broken up by heat, carbon dioxide being evolved, and the normal carbonate left behind. Being insoluble, the precipitate of chalk has no action upon soap—hence the fact that hard water is (usually) softened by boiling. The action that takes place when water containing carbon dioxide in solution acts upon chalk may be expressed by the equation—

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2$$

When the solution is boiled the action is simply reversed, thus—

$$CaH_2(CO_3)_2 = CaCO_3 + H_2O + CO_2$$

Ex. 163.—Find out whether a similar change occurs when a solution of sodium bicarbonate is boiled.

159. Permanently Hard Water.—It has been said that hard

water is *usually* softened by boiling. But there are many hard waters which are only partially softened, and some that are not softened at all by boiling. In these cases it is usually found on evaporating the water that the residue left consists of calcium sulphate. This salt is not altered by boiling, but it acts upon soap in exactly the same way as calcium bicarbonate. Hence water containing calcium sulphate is called "permanently hard," while water which contains only calcium bicarbonate is known as "temporarily hard."

Ex. 164.—Procure a sample of permanently hard water. Evaporate some of it to dryness, and test the residue for calcium by the flame test, and for a sulphate by adding hydrochloric acid and a few drops of barium chloride solution.

Ex. 165.—Dissolve some calcium sulphate in distilled water. Take 20 c.c. of the clear solution, and find how much soap solution it requires to give a permanent lather. Boil another portion of the solution, take 20 c.c., and again test it with the soap solution. Do you find any difference?

160. Gases dissolved in Water.—We have learned from Ex. 160 that natural waters contain dissolved gases. These gases are derived from the atmosphere, but the proportion between the oxygen and nitrogen is very different from that in air, being about two volumes of nitrogen to one of oxygen, instead of four to one as in air. This is exactly what might be expected in view of the fact that the solubility of oxygen is about double that of nitrogen. It is also an additional proof that air is a mixture and not a compound of the two gases, for a compound would, of course, dissolve as a whole, and without any alteration in the proportion between its constituents.

The air dissolved in water is of great importance to fishes and other animals that breathe by gills. These creatures require oxygen to aerate their blood just as we do, but they can only make use of it when it has been previously dissolved in water. Hence a fish will die in a few minutes if placed in water that has been deprived of its dissolved air by continued boiling.

161. Other Salts in Natural Waters.—Besides the acid carbonate and sulphate of calcium (and less frequently of magnesium), river and spring waters contain other salts. The most important of these is common salt.

The following table gives the approximate[1] composition of the residue left on evaporating one gallon of three typical waters :—

	Moorland Water.	Well Water (in Chalk).	Sea Water.
Calcium Carbonate . .	1·7	14·1	...
Calcium Sulphate . .	...	1·8	91
Magnesium Carbonate .	...	...	...
Magnesium Sulphate .	1·7	1·4	140
Magnesium Chloride .	...	...	220
Potassium Chloride . .	...	...	51
Sodium Chloride . .	0·9	1·8	1868
Sodium Sulphate . .	...	...	...
Sodium Nitrate . .	...	1·4	...
Total (grains per gallon) .	4·3	20·5	2370

162. Sea Water.—The analyses given above show that the composition of sea water differs in a very marked manner from that of other natural waters. The latter almost always contain calcium salts in comparatively large quantities, while salts of other metals are present only in much smaller amount. In sea water, on the other hand, there is only a small proportion of calcium salts, and by far the largest proportion of the white residue left on evaporation consists of common salt. The reason is that the calcium carbonate is removed from sea water by the countless myriads of marine shell-forming animals which use it to build up their shells. The common salt is not removed, and consequently has gradually accumulated until, as we have seen, it has reached the comparatively large proportion of about 27 gm. in each litre of sea water. There is little doubt that the proportion of salt will go on increasing, but the rate of increase is so slow, and the discovery of accurate analytical methods so recent, that as yet we cannot say what the rate of increase is. In certain inland seas which have no outlet (the Dead Sea in Palestine, for example), the proportion of salt has become so great that the point of saturation is being approached, and solid salt is being deposited in large

[1] The less important constituents have been omitted.

quantities around the margin. There is little doubt that this is the manner in which the beds of rock salt found in Cheshire, in Galicia, and elsewhere have been formed. The proportion of dissolved salts in sea water is so large as to influence very considerably the physical properties of the liquid. Thus its specific gravity is decidedly higher than that of pure water (about 1·026), its point of maximum density is below 4° C., and its freezing point—or, rather, the temperature at which ice begins to form in it—is about − 2·5° C.

QUESTIONS AND EXAMPLES ON CHAPTER XIII.

1. Name three common alkalies. What elements are contained in each of them? Give an equation for the action of hydrochloric acid on each.

2. How could you convert metallic copper into copper hydrate? What happens when the latter substance is heated? Give equations.

3. How is ammonia gas prepared? Sketch the apparatus you would use for collecting a jar of *dry* ammonia.

4. Ammonia gas is passed through a weighed tube containing heated copper oxide. If the oxide loses 0·80 gm. in weight, what volume of nitrogen (at N.T.P.) should be set free?

5. What happens when ammonia gas is passed into nitric acid? Compare the reaction with that which takes place when caustic soda and nitric acid are brought together.

6. How could you distinguish ammonium sulphate from (*a*) potassium sulphate, (*b*) ammonium chloride?

7. What is meant by ammonium hydrate? Write an equation for the action of this substance on sulphuric acid.

8. If ammonium sulphate were heated with quicklime what action would take place? Give an equation and suggest an experiment by which the correctness of the equation might be tested.

9. What is meant by a standard solution? How would you prepare a standard solution of sodium carbonate?

10. What is an acid salt? Write the formula of acid potassium carbonate. What percentage of carbon does it contain?

11. How would you test a sample of hard water to find out whether it is permanently or temporarily hard? To what is the hardness probably due in each case?

12. A sample of permanently hard water gives a white precipitate with barium chloride and hydrochloric acid. What can you infer from this? How would you decide whether the metal present is calcium or magnesium?

13. Explain exactly how air that has been dissolved in water differs from ordinary air. What bearing has its composition upon the question whether air is a mixture or a compound?

14. Temporarily hard water is sometimes softened by adding lime-water to it. Can you suggest what happens? (See par. 153.)

15. When electric sparks are passed through ammonia gas it is broken up into nitrogen and hydrogen. Calculate from the formula NH_3 and the relative density of the two gases what volume of each would be formed (at N.T.P.) from 17 gm. of ammonia.

16. A flask of 1 litre capacity weighed 26·790 gm. when full of air, and 26·265 gm. when full of ammonia, both at N.T.P. Calculate the relative density of ammonia when that of hydrogen = 1.

APPENDIX

GLASS WORKING AND FITTING UP APPARATUS

1. To cut Glass Tubing.—Make a scratch across the tube with a *sharp* triangular file. Then hold the tube with one hand on each side of the scratch, and about half-an-inch away from it, and bend the tube away from the scratched side. It will break at the scratch. In the case of tubes of more than about 1 cm. diameter the scratch must be carried right round the tube.

2. To bend Glass Tubing.—Hold the tube, as shown in the figure, in the upper part of an ordinary fish-tail gas jet,[1] so that a length of 5 or 6 cm. is heated. Keep turning the tube on its axis so that all sides are heated equally, and continue this for a minute or so after the glass begins to soften. Then remove the tube from the flame, and without using any force allow one end to fall over to the angle required.

Fig. 72.

3. To seal one end of a Glass Tube.—Hold one end of the tube in the extreme edge of the blowpipe or Bunsen flame and keep constantly revolving it. The sides of the opening will gradually contract to a very small hole and at last will close up altogether. When this point is reached blow cautiously into the open end of the tube (using the pressure from the cheeks only, *not* from the lungs) so as to slightly expand the lump of melted glass at the closed end.

[1] When gas is not available, the flame of a Wanzer or other chimneyless paraffin lamp may be used.

4. To draw out a Glass Tube to a fine Jet.—Heat the part to be drawn out in the blowpipe flame, revolving it constantly, and at the same time pressing the two ends together *very slightly*. The sides of the heated part will gradually thicken and contract, and if the process be continued would close up altogether. Before this point is reached, the tube is removed from the flame, and the ends gently drawn apart, *the tube being still constantly revolved during the whole process*, so long as the glass remains soft. In the case of a tube of small diameter this operation may be carried out with an ordinary Bunsen. The flame should be protected from draught by a chimney and the extreme top of the flame should be used.

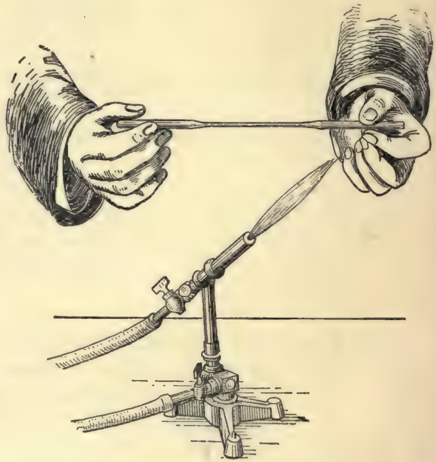

Fig. 73.

5. To blow a Bulb.—Seal one end of a tube as already described. Continue heating in the blowpipe flame until about half-an-inch of the tube is at a bright red heat. Take the tube out of the flame (revolving it constantly while doing so), hold it vertically with the open end upwards and blow into it, using the pressure from the cheeks only (as in pronouncing the letter P), not from the lungs. If the resulting bulb is too small or badly shaped, it may be re-heated in the yellow flame got by sending a very gentle current of air through the blowpipe. If constantly rotated in this flame the bulb will gradually shrink in size without wrinkling, as it would if heated in the blue "roaring" flame. The heat may then be gradually increased as the sides of the bulb

become thicker, and at last the tube may be taken out of the flame and another attempt made to blow the bulb. The chief points to be observed are:

(1) That the glass must be constantly rotated.

(2) That the pressure of air used in blowing the bulb must be carefully regulated.

6. To make a Mercury Funnel from a Test-tube (this is useful for introducing mercury into the volumeter—see p. 92).—Take an ordinary half-inch test-tube, heat the centre portion in the comparatively cool yellow flame got by working the bellows very gently. Continue to heat and rotate the tube until the centre portion has contracted to half its original diameter. Increase the heat for a little. Remove the tube from the flame and draw it out slowly, rotating it all the time. Cut off the narrow tube about 8 cm. from the mouth.

7. To make a short Test-tube from a long one.—The method of heating is the same as in the last operation, but the tube is drawn out *in the flame*. The latter is kept always at that part of the narrowed tube which is next to the open end of the test-tube, so that as much as possible of the waste glass in the centre may be drawn away. When the tube has been sealed, the end is more strongly heated and then carefully blown into shape. If an irregular lump of glass has been allowed to remain at the end, the heating and blowing out may require to be repeated several times.

8. To make a hard glass Test-tube.—Take a piece of Jena tubing of suitable diameter and about 24 cm. long. Heat in the middle, using the hottest blowpipe flame that you can get, and as soon as the glass softens draw out in the flame as in the last experiment. Round the end as before, and repeat the operations with other half of the tube, using the waste glass as a handle. Lastly heat the open end of each tube in the edge of a large "roaring" flame till the glass softens. The edge may be turned out by inserting, while the glass is hot, a piece of charcoal shaped like a cone. In working with thick-walled tubing care must be taken not to put it suddenly into a hot flame. It should be first gradually heated in the smoky flame.

9. To bore a Cork. — Select a good cork free from flaws. Squeeze it several times in a press or tongs sold for the purpose; or if neither of these is available, wrap it in paper and roll it under your foot till it becomes quite soft. Take a sharp cork-borer of the same diameter as the tube which is to pass through the hole, or very slightly thicker. Begin at the narrow end of the cork and pass the cork-borer in with a screwing motion, constantly turning the cork round in the left hand so as to make sure that the direction of the hole is kept parallel to the axis of the cork. On no account should the cork-borer be forced through roughly, or the cork pressed against the table—the result of this would be a ragged hole which could not make a tight joint. The cork-borer must be frequently sharpened with an instrument sold for the purpose.

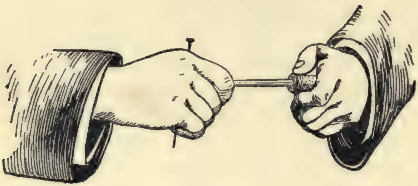

Fig. 74.

India-rubber stoppers may be bored in the same way with a wetted cork-borer, but are better bought ready bored. In passing a tube through the hole in a cork or india-rubber stopper the tube should first be wetted or slightly greased with vaseline. The tube should be held as close to the cork as possible, and *on no account should pressure be applied at or beyond a bend.* The sharp edges of the tube must be removed by holding it in the edge of the Bunsen flame, or by the use of a file, before trying to pass it through the cork.

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